

Born-Oppenheimer potential for HeH⁺

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We demonstrate high accuracy calculations for the HeH⁺ molecule using analytic formulas for two-center two-electron integrals with exponential functions. The Born-Oppenheimer potential for the ground electronic $^1\Sigma^+$ state is obtained in the range of 0.1–60 a.u. with precision of about 10^{-12} a.u. As an example, at the equilibrium distance between nuclei $r_e = 1.463\,283$ a.u., the Born-Oppenheimer potential amounts to $-2.978\,708\,310\,771(1)$ a.u. Obtained results lay the ground for theoretical predictions in HeH⁺ with spectroscopic precision.

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I. INTRODUCTION

The HeH⁺ molecule is a simple two-electron molecule consisting of the α particle and the proton as nuclei. In the ground electronic $^1\Sigma^+$ state, both electrons are mostly centered around the α nucleus with the proton distance from α being about $r \approx 1.46$ a.u. The first accurate variational calculations of the Born-Oppenheimer (BO) potential of HeH⁺ reported by Wolniewicz [1], Kołos and Peek [2], and Kołos [3], were shortly afterward refined by Bishop and Cheung [4]. In these calculations the authors represented the electronic wave function in terms of exponential functions times various polynomials in interparticle distances with general nonlinear parameters (Kołos-Wolniewicz functions) or with some parameters fixed (James-Coolidge functions). The accuracy achieved in calculations by Bishop and Cheung was about 4×10^{-6} a.u. More accurate results, $\sim 10^{-8}$ a.u., at the distance $r = 1.46$ a.u., have been obtained by Cencek *et al.* [5] using explicitly correlated Gaussian functions. Even if the whole BO potential is known with their accuracy (~ 0.02 cm⁻¹), it will be insufficient in comparison with the most accurate ($\sim 10^{-5}$ cm⁻¹) measurements of rovibrational transition frequencies [6]. More recently Adamowicz *et al.* [7–9] performed direct nonadiabatic calculations for HeH⁺ including relativistic corrections, however, only for purely vibrational states and without estimation of accuracy.

In this work we use asymptotically correct generalized Heitler-London functions, which are the product of an exponential atomic He function times an arbitrary polynomial in interparticle distances. Thanks to analytic formulas for the resulting two-center two-electron integrals [10], we are able to perform calculations with a large number of $\sim 20\,000$ basis functions. The resulting accuracy of $\sim 10^{-12}$ a.u. or better (for large distances) is at least four orders of magnitude improvement with respect to previous values. The accuracy of the BO potential is not directly transformed into accuracy of rovibrational energy levels. It is because Born-Oppenheimer energies should be supplemented by adiabatic, nonadiabatic, relativistic, and QED corrections. As it has been recently demonstrated for H₂ and isotopomers [11], the perturbative treatment in the electron-nuclei mass ratio up to $O((m/M)^2)$ and the fine-structure constant α up to $O(\alpha)^3$ can provide rovibrational transitions with accuracy reaching 0.0001 cm⁻¹. Analogous calculations can be performed for HeH⁺, and results obtained here are the first step for spectroscopically accurate theoretical predictions.

II. EXPLICITLY CORRELATED ASYMPTOTIC BASIS SET

We represent the ground-state nonrelativistic electronic wave function in terms of generalized Heitler-London functions, which are the product of the atomic He exponential function with an arbitrary polynomial in all interparticle distances,

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

such that

$$\sum_{i=1}^5 n_i \leq \Omega \quad (2)$$

for some integer Ω , and call them the explicitly correlated asymptotic (ECA) basis. In the above, $c_{\{n\}}$ are linear coefficients, $\{n\}$ represents a set of five numbers $\{n_1, n_2, n_3, n_4, n_5\}$, P_{12} is the operator which replaces \vec{r}_1 with \vec{r}_2 , indices (A, B) denote nuclei, and $(1, 2)$ denote electrons. Matrix elements of the nonrelativistic Hamiltonian can be expressed in terms of integrals of the form

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

with nonnegative integers n_i . These integrals depend on the nonlinear parameter β and on the distance $r \equiv r_{AB}$ between nuclei. They are calculated as follows. When all $n_i = 0$, the so-called master integral, which can be derived from a general expression in Ref. [10], is

$$f(r, \beta) = \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-\beta r_{1A}}}{r_{1A}} \frac{1}{r_{1B}} \frac{e^{-\beta r_{2A}}}{r_{2A}} \frac{1}{r_{2B}} \frac{r}{r_{12}} = \frac{1}{\beta^2} \int_0^{\beta r} dx F(x) = -\frac{1}{\beta^2} \int_{\beta r}^{\infty} dx F(x). \quad (4)$$

with

$$F(x) = \frac{1}{x} \left[\frac{e^{2x}}{2} \text{Ei}(-2x) - \frac{e^{-2x}}{2} \text{Ei}(2x) - \text{Ei}(-x) + e^{-2x} \text{Ei}(x) \right], \quad (5)$$

where Ei is the exponential integral function. The one-dimensional integral in Eq. (4) is calculated numerically using the adapted Gaussian integration. With 120 integration points

one achieves 64 significant digits for all the distances. All f integrals with higher powers of electron distances can be obtained from recursion relations, which were derived in Ref. [10]. Since

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

it is sufficient to know f integrals at $r = 1$ only; values at arbitrary r are obtained by rescaling β and f according to the above formula. As an example and demonstration of the computational method, we present below formulas at $r = 1$ for all f integrals with $\sum_i n_i \leq 2$,

$$\begin{aligned} f(0,0,0,0,0) &= f, \\ f(0,0,0,0,1) &= \frac{1}{2\beta^3} + \frac{e^{-2\beta}}{2\beta^3} - \frac{e^{-\beta}}{\beta^3} + \frac{[\text{Ei}(-2\beta) - \text{Ei}(-\beta)]}{\beta^2}, \\ f(0,0,0,1,0) &= -\frac{F}{2\beta^3} + \frac{f}{\beta}, \\ f(1,0,0,0,0) &= \frac{1}{\beta^4} + \frac{e^{-2\beta}}{\beta^4} - \frac{2e^{-\beta}}{\beta^4}, \\ f(0,0,0,0,2) &= \frac{1}{2\beta^3} - \frac{e^{-\beta}}{\beta^3} - \frac{\text{Ei}(-\beta)}{\beta^2} + \frac{f}{\beta^2}, \\ f(0,0,0,1,1) &= \frac{3}{4\beta^4} + \frac{5e^{-2\beta}}{4\beta^4} \\ &\quad - \frac{2e^{-\beta}}{\beta^4} + \frac{2[\text{Ei}(-2\beta) - \text{Ei}(-\beta)]}{\beta^3}, \\ f(0,0,0,2,0) &= -\frac{e^{-\beta}}{2\beta^3} + \frac{e^{2\beta}\text{Ei}(-2\beta)}{2\beta^3} - \frac{(1+\beta)\text{Ei}(-\beta)}{2\beta^3} \\ &\quad - \frac{(5+2\beta)F}{4\beta^4} + \frac{2f}{\beta^2}, \\ f(0,0,1,0,1) &= \frac{1}{2\beta^3}, \\ f(0,0,1,1,0) &= \frac{3}{4\beta^4} + \frac{e^{-2\beta}}{4\beta^4} - \frac{e^{-\beta}}{\beta^4}, \\ f(0,1,0,1,0) &= \frac{e^{-\beta}}{2\beta^3} + \frac{e^{2\beta}\text{Ei}(-2\beta)}{2\beta^3} + \frac{(1-\beta)\text{Ei}(-\beta)}{2\beta^3} \\ &\quad - \frac{(5+2\beta)F}{4\beta^4} + \frac{f}{\beta^2}, \\ f(1,0,0,0,1) &= \frac{1}{\beta^4} - \frac{e^{-\beta}}{\beta^4}, \\ f(1,0,0,1,0) &= \frac{2}{\beta^5} + \frac{(2+\beta)e^{-2\beta}}{\beta^5} - \frac{(4+\beta)e^{-\beta}}{\beta^5}, \\ f(2,0,0,0,0) &= \frac{2}{\beta^5} - \frac{2(1+\beta)e^{-\beta}}{\beta^5} - \frac{2e^{2\beta}\text{Ei}(-2\beta)}{\beta^5} \\ &\quad + \frac{2(1+\beta)\text{Ei}(-\beta)}{\beta^5} + \frac{(1+2\beta)F}{\beta^6} + \frac{2f}{\beta^2}, \quad (7) \end{aligned}$$

where $f = f(1, \beta)$ and $F = F(\beta)$. Other f integrals from the same shell can be obtained by using the symmetry $f(n_1, n_2, n_3, n_4, n_5) = f(n_1, n_4, n_5, n_2, n_3)$. Integrals with higher powers n_i are of analogous form; they are all linear combinations of f , F , Ei , \exp , and identity functions with coefficients being simple polynomials in $1/\beta$. Using a

computer symbolic program and prescription from Ref. [13], we have generated a table of integrals with $\sum_i n_i \leq 37$, which corresponds to a maximum value of $\Omega = 16$.

III. NUMERICAL RESULTS

The matrix elements of the nonrelativistic Hamiltonian between ECA functions are obtained as described by Kołos and Roothaan in [12]. The resulting expression is a linear combination of various ECA integrals which are calculated by using analytic formulas as presented in the previous section. Their evaluation is fast and accurate, thus suitable for calculations involving a large number of basis functions.

Eigenvalues of the Hamiltonian matrix are obtained by inverse iteration method for various lengths of basis sets ($\Omega = 7-16$). These eigenvalues, obtained at 132 internuclear distances ranging from 0.1 to 60 a.u., form the BO potential. ECA functions are especially suitable for large distances, as they include functions for the helium atom alone. As a result, the atomic He energy is obtained with an accuracy of about 10^{-15} for all the distances, in fact much better than that for HeH^+ . In order to improve numerical accuracy for HeH^+ , we used a triple basis set ($\Omega, \Omega - 2, \Omega - 4$) each one with its own optimized nonlinear parameter α . Numerical calculations are performed for $r \leq 12$ a.u. using quadruple precision arithmetic, whereas for $r > 12$ a.u. they are performed using octuple precision arithmetic. In order to check numerics, we repeated calculations around the equilibrium distance $r_e = 1.463\,283$ a.u. by using the James-Coolidge basis set, for which analytic formulas have been developed in Ref. [13]. This basis has a slower convergence but is numerically more stable, so we could use an even larger number of 27 334 basis functions. Obtained results have similar accuracy and are in perfect agreement with that obtained with ECA functions. The most accurate variational result reported at the distance $r = 1.46$ a.u. is compared in Table I to all the previous results obtained so far in the literature.

In performing extrapolation to a complete basis set ($\Omega \rightarrow \infty$), similarly to the previous H_2 case [13], we observe the exponential $e^{-\beta\Omega}$ convergence, in other words the logarithm of differences in energies for subsequent values of Ω fits well to a linear function. This makes extrapolation to infinity quite simple. Extrapolated results for the whole BO potential curve in the range 0.1–60 a.u. are presented in Table II.

IV. SUMMARY

We have demonstrated applications of analytic formulas for two-center two-electron exponential integrals in

TABLE I. Variational Born-Oppenheimer potential for the HeH^+ molecule at $r = 1.46$ a.u.

Authors	Energy (a.u.)
1965 Wolniewicz [1]	-2.978 666 7
1994 Kołos and Peek [2]	-2.978 689 06
1979 Bishop and Cheung [4]	-2.978 702 62
2006 Cencek, Komasa, and Rychlewski [5]	-2.978 706 591
2012 This work	-2.978 706 600 341

TABLE II. Numerical values for the BO potential at different internuclear distance r , shifted by the He ground-state energy $E = -2.903\,724\,377\,034\,120$ a.u. Results are obtained by extrapolation to the complete set of basis functions; $r_e = 1.463\,283$ a.u. is the equilibrium distance.

$r/\text{a.u.}$	E	$r/\text{a.u.}$	E	$r/\text{a.u.}$	E	$r/\text{a.u.}$	E
0.10	15.765 275 621 061(3)	1.60	-0.072 566 613 147(4)	3.25	-0.010 505 993 345 15(2)	5.80	-0.000 684 274 833 49(5)
0.20	6.050 585 777 587 9(4)	1.65	-0.070 782 049 442(4)	3.30	-0.009 805 291 916 24(2)	5.90	-0.000 634 959 821 45(7)
0.30	3.035 104 004 312 9(1)	1.70	-0.068 681 986 181(4)	3.35	-0.009 153 886 966 24(2)	6.00	-0.000 590 184 825 0(1)
0.40	1.676 798 340 477 6(1)	1.75	-0.066 346 472 331(4)	3.40	-0.008 548 577 089 50(2)	6.20	-0.000 512 278 183 5(1)
0.50	0.961 224 244 974 8(1)	1.80	-0.063 841 750 276(3)	3.45	-0.007 986 304 940 94(2)	6.40	-0.000 447 216 535 6(6)
0.60	0.551 425 923 210 9(2)	1.85	-0.061 222 573 648(3)	3.50	-0.007 464 161 626 98(2)	6.60	-0.000 392 456 561 3(6)
0.70	0.305 137 807 453 6(3)	1.90	-0.058 534 109 374(3)	3.55	-0.006 979 388 833 37(2)	6.80	-0.000 346 039 248 5(6)
0.80	0.153 061 340 049 4(5)	1.95	-0.055 813 503 899(3)	3.60	-0.006 529 379 042 23(2)	7.00	-0.000 306 439 293 9(6)
0.90	0.058 077 362 203 3(8)	2.00	-0.053 091 177 182(2)	3.65	-0.006 111 674 157 71(2)	7.20	-0.000 272 456 681 9(6)
0.95	0.024 964 448 474 0(9)	2.05	-0.050 391 895 330(2)	3.70	-0.005 723 962 825 47(2)	7.40	-0.000 243 137 960 03(5)
1.00	-0.001 080 054 475(1)	2.10	-0.047 735 662 718(2)	3.75	-0.005 364 076 701 23(2)	7.60	-0.000 217 718 542 45(4)
1.05	-0.021 440 483 674(2)	2.15	-0.045 138 466 546(2)	3.80	-0.005 029 985 892 14(2)	7.80	-0.000 195 580 003 55(3)
1.10	-0.037 213 297 730(2)	2.20	-0.042 612 900 482(1)	3.85	-0.004 719 793 768 31(2)	8.00	-0.000 176 218 146 92(3)
1.15	-0.049 273 330 916(2)	2.25	-0.040 168 689 007(1)	3.90	-0.004 431 731 314 03(2)	8.50	-0.000 137 416 959 04(5)
1.20	-0.058 323 089 351(2)	2.30	-0.037 813 130 017 8(9)	3.95	-0.004 164 151 165 85(2)	9.00	-0.000 108 799 429 7(1)
1.25	-0.064 929 882 196(3)	2.35	-0.035 551 469 970 6(7)	4.00	-0.003 915 521 460 65(2)	9.50	-0.000 087 296 341 4(7)
1.30	-0.069 554 101 696(3)	2.40	-0.033 387 223 169 6(6)	4.10	-0.003 469 526 010 47(2)	10.0	-0.000 070 874 764(5)
1.35	-0.072 570 979 391(3)	2.45	-0.031 322 444 662 9(5)	4.20	-0.003 083 563 658 79(2)	10.5	-0.000 058 152 803(6)
1.38	-0.073 739 700 599(4)	2.50	-0.029 357 964 421 4(4)	4.30	-0.002 748 907 761 76(2)	11.0	-0.000 048 170 045(4)
1.40	-0.074 287 476 582(4)	2.55	-0.027 493 589 050 7(3)	4.40	-0.002 458 102 556 14(2)	11.5	-0.000 040 245 989 5(9)
1.41	-0.074 497 742 079(2)	2.60	-0.025 728 276 107 6(2)	4.50	-0.002 204 793 867 58(2)	12.0	-0.000 033 890 131 5(2)
1.42	-0.074 667 994 434(2)	2.65	-0.024 060 285 148 3(2)	4.60	-0.001 983 576 228 38(2)	13.0	-0.000 024 539 525 11(1)
1.43	-0.074 799 949 340(2)	2.70	-0.022 487 308 864 0(1)	4.70	-0.001 789 856 934 04(3)	14.0	-0.000 018 206 960 42(1)
1.44	-0.074 895 257 253(1)	2.75	-0.021 006 587 043 5(1)	4.80	-0.001 619 736 634 04(3)	15.0	-0.000 013 793 858 65(1)
1.45	-0.074 955 506 003(1)	2.80	-0.019 615 005 609 25(9)	4.90	-0.001 469 905 474 75(3)	16.0	-0.000 010 641 724 04(1)
1.46	-0.074 982 223 308(1)	2.85	-0.018 309 182 582 72(7)	5.00	-0.001 337 553 485 43(4)	17.0	-0.000 008 341 461 47(1)
r_e	-0.074 983 933 737(1)	2.90	-0.017 085 542 525 64(6)	5.10	-0.001 220 293 751 56(4)	18.0	-0.000 006 630 920 31(1)
1.47	-0.074 976 879 155(1)	2.95	-0.015 940 380 764 26(5)	5.20	-0.001 116 096 895 45(4)	19.0	-0.000 005 337 497 57(1)
1.48	-0.074 940 888 099(1)	3.00	-0.014 869 918 514 72(4)	5.30	-0.001 023 235 434 23(4)	20.0	-0.000 004 344 797 44(1)
1.49	-0.074 875 611 446(1)	3.05	-0.013 870 349 882 66(3)	5.40	-0.000 940 236 685 33(4)	30.0	-0.000 000 855 679 62(1)
1.50	-0.074 782 359 346(1)	3.10	-0.012 937 881 595 48(3)	5.50	-0.000 865 843 012 73(5)	40.0	-0.000 000 270 476 79(1)
1.52	-0.074 516 925 580(3)	3.15	-0.012 068 766 236 41(3)	5.60	-0.000 798 978 332 42(5)	50.0	-0.000 000 110 738 51(1)
1.55	-0.073 938 987 047(4)	3.20	-0.011 259 329 676 92(2)	5.70	-0.000 738 719 940 4(4)	60.0	-0.000 000 053 391 46(1)

high-precision calculations of Born-Oppenheimer potential for the ground electronic state of HeH⁺, similarly to previous calculations for H₂ [13]. The use of the ECA basis with as many as 20 000 functions provided energies with a precision of $\sim 10^{-12}$ – 10^{-14} a.u. for internuclear distances up to 60 a.u.

The extension of this approach to calculations of excited states of diatomic molecules such as H₂ and HeH⁺ is not difficult. As long as the trial function includes at most two different nonlinear parameters (in the exponent), the analytic formulas for corresponding integrals are not exceedingly large. Such two-parameter exponential functions can represent well an arbitrary electronic state of a diatomic molecule.

In fact, we aim to develop a general code for calculation of the BO potential of the diatomic molecule, using quad and arbitrary precision arithmetic. The extension to adiabatic, nonadiabatic, and relativistic corrections is more problematic. For their evaluation one needs integrals with inverse powers of interparticle distances, for which formulas can be quite complicated. We think that their derivation for the James-Coolidge basis is within reach, therefore for small internuclear distances, where this basis works quite well, all relevant corrections, including yet unknown α^4 QED correction can be calculated to a high precision, thus improving theoretical predictions for H₂ and other two-electron diatomic molecules to $\sim 10^{-6}$ cm⁻¹.

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