Precise nonvariational calculation of excited states of helium with the correlation-function hyperspherical-harmonic method

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A direct solution of the Schrödinger equation for the $2\,^1S$, $3\,^1S$, $4\,^1S$, and $5\,^1S$ states of the helium atom is obtained with the correlation-function hyperspherical-harmonic (CFHH) method. Given the proper correlation function chosen from physical considerations, the method generates wave functions accurate in the whole range of interparticle distances that lead, in turn, to precise estimates of the expectation values of the Hamiltonian and of different functions of interparticle distances. Our results show that even with the simplest correlation function, the accuracy of the CFHH method (which contains no adjustable parameters) for excited states is comparable to that of the ground state. The accuracy is also comparable to that of the most sophisticated variational calculations involving hundreds of variational parameters.

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The correlation-function hyperspherical-harmonic (CFHH) method, unifying the correlation-function approach [1] with the hyperspherical-harmonic method [2], was introduced a few years ago by Haftel and Mandelzweig [3–8]. The method provides a very accurate direct solution of the Schrödinger equation for different three-body systems and cures the main pitfall of the variational method—the necessity of guessing the mathematical form of the wave function, which can result in a low-quality wave function even in cases where hundreds of variational parameters generate extremely precise energies [9]. Given the proper correlation function, chosen from physical considerations, the CFHH method yields wave functions accurate in the whole range of interparticle distances [8]. This leads, in turn, to precise estimates of the expectation values of the Hamiltonian and of different functions of interparticle distances [4–7]. Variational wave functions, on the other hand, are often accurate only in the region where the probability density is high. The Green's-function Monte Carlo method, which is applied, for example, to calculate the ground state of the three-body mesomolecular $dt\mu$ system [10], does not have these limitations, but its extension to the excited states is very difficult because any small admixture of the ground state in the importance function will eventually dominate the numerical simulation.

To date the accuracy of the CFHH method has been verified for ground ($1\,^1S$) and first excited ($2\,^1S$) states of the helium atom [3,4,6,8], for the ground states of mesomolecular $pp\mu$, $dd\mu$, and $tt\mu$, systems [7], and for the ground state of the positronium negative ion $e^-e^-e^+$ (also denoted Ps^-) [5,8]. These calculations demonstrate the utility of the method in systems with different mass ratios. The direct bound-state solution [3–8] of the Schrödinger equation obtained by the CFHH method has yielded precision comparable to that obtained previously only by elaborate variational calculations. For example, for maximum global momentum $K_m=48$, up to nine-significant-figure precision is obtained for the energy of the $1\,^1S$ and $2\,^1S$ states of the helium atom [4,6] and seven significant figures for the positronium ion [5]. The wave functions for the whole range of the interparticle distances and different expectation values for these systems have about six- and five-significant-figure precision, respectively, and the overall and local quality of the corresponding wave functions is very high [8].

In this paper we extend our study of the CFHH method to the $3\,^1S$, $4\,^1S$, and $5\,^1S$ states of the helium atom. This is our first application of the method to highly excited states. In order to improve the accuracy of the calculations we increase here the value of maximum global momentum up to $K_m=56$. This increases from 169 to 225 the number of basis hyperspherical-harmonic functions and the corresponding coupled equation. Since the previous $2\,^1S$ CFHH computation with cusp parameters [8] only included expectation values of the Hamiltonian and of the relative local deviation $\Delta=(H\psi/E\psi)-1$ (which defines the quality of the wave function [11]), in the present work we generate the complete results for the $2\,^1S$ excited state including expectation

values of different functions of interparticle distances.

In the CFHH method [2–8] we write the wave function as a product of two factors

$$\psi=\chi\phi\ , \tag{1}$$

where χ is the "correlation function" and ϕ is expanded in the usual hyperspherical-harmonic (HH) functions. If the correlation function χ is chosen to describe the singular features of ψ (like cusps), the HH expansion for ϕ should be rapid. The solution for ϕ proceeds as in the usual HH method, except the potential V is replaced by an effective velocity-dependent potential V'

$$V'=V-\frac{1}{2}\frac{\nabla^2\chi}{\chi}-(\nabla\ln\chi)\nabla\ , \tag{2}$$

where ∇ is the six-dimensional gradient operator and V in our case is a sum of the pair Coulomb potentials. In the present calculation of the helium excited states we will employ as before [2–4,6] the simplest spatially symmetric correlation function

$$\chi=\exp(f),\quad f=-\gamma(r_{13}+r_{23})-\delta r_{12}\ , \tag{3}$$

with the cusp parametrization $\gamma=2$, $\delta=-0.5$, which generates very accurate wave functions [8] for the ground and first excited states. Here particle 3 is the helium nucleus, whose mass here, for the sake of comparison with the variational calculations [12–16,28], is presumed infinite. We shall see that the very simple choice (3) leads to surprisingly accurate wave functions also for higher excited states.

The spatial extent of the wave function in the hyperspherical radial variable [6,17–20] ρ,

$$\rho^2=\frac{1}{(M+2)}[r_{12}^2+M(r_{13}^2+r_{23}^2)]\ , \tag{4}$$

satisfying the Schrödinger equation for three Coulomb particles [expressed below in the atomic units (a.u.), which are used throughout the paper]

$$\left[\frac{1}{2}(\Delta_1+\Delta_2)+\frac{1}{2M}\Delta_3+E-\frac{Z_1Z_3}{r_{13}}-\frac{Z_2Z_3}{r_{23}}-\frac{Z_1Z_2}{r_{12}}\right]\psi=0 \tag{5}$$

depends on the excited state one has to calculate. In order to estimate this range for the excited helium atom, consider a scalar solution of the equation with infinite mass M (whose center of mass is located at $\mathbf{r}_3=0$) when particles 1 and 2 do not interact. Up to a normalization constant one obtains [21]

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2),\quad E=E_1+E_2\ , \tag{6}$$

where

$$\psi_i(\mathbf{r}_i)=e^{-r_i/n_ia_i}L^1_{n_i-1}\left[\frac{2r_i}{n_ia_i}\right]\ ,$$

$$a_i=-\frac{1}{Z_iZ_3}\ ,\quad E_i=-\frac{1}{2n_i^2a_1^2}\ .$$

Here n_i is an excitation number of the particle i. Since for small x the Laguerre polynomial $L^1_{n-1}(x)$ is proportional [22] to $1-(n-1)/2x$, we have that in the cusp region $r_i\ll a_i$

$$\psi(\mathbf{r}_1,\mathbf{r}_2)\approx 1-\frac{r_1}{a_1}-\frac{r_2}{a_2}\ ,$$

which means that the Kato cusp condition [23]

$$\frac{1}{\psi}\left[\frac{\partial\psi}{\partial r_i}\right]_{r_i\to 0}=Z_iZ_3$$

is satisfied. The asymptotic region starts when the wave function of the i-th electron decays exponentially, that is when $\psi_i(r_i)\approx e^{-r_i/n_ia_i}L^1_{n_i-1}(2r_i/n_ia_i)$ is proportional to $e^{-\sqrt{2|E_i|}r_i}=e^{-r_i/n_ia_i}$. Since the largest term in $L^1_{n_i-1}(2r_i/n_ia_i)$ is

$$\left[\frac{2r_i}{n_ia_i}\right]^{n_i-1}=\exp\left[(n_i-1)\ln\frac{2r_i}{n_ia_i}\right]\ ,$$

the asymptotic region starts when $(n_i-1)\ln 2r_i/n_ia_i \ll r_i/n_ia_i$. Neglecting the slowly varying logarithmic factor (of order of unity) we obtain $r_i\gg n_i(n_i-1)a_i$ defining the asymptotic region.

For the singly excited nS helium state (where $Z_1=Z_2=-1$, $Z_3=2$, $n_1=1$, and $n_2=n$) one has therefore the following asymptotic condition for a coordinate r_2 of an excited electron: $r_2\gg n(n-1)/2$. Consequently, since asymptotically $r_2\gg r_1$ (r_1 is a coordinate of the electron in the ground state), the asymptotic condition for ρ, defined by Eq. (4), is

$$\rho\gg\frac{n(n-1)}{2\sqrt{2}}\ . \tag{7}$$

The numerical accuracy of our calculations is determined by the precision of the following procedures: (i) computation of matrix elements of the effective potential V', (ii) solution of the system of N coupled second-order radial differential equations, (iii) summations and numerical integrations in the process of calculating different expectation values.

Since (i) and (ii) were done mostly analytically [6,17,24,25] (only the part of the calculation that can be easily handled by the computer has to be performed numerically, such as computing some matrix elements [6] and the recurrence coefficients [24,25]), their precision is very high, 10^{-13} and 10^{-11}, respectively, for the $2\,^1S$ and $3\,^1S$ excited states and 10^{-13} and 10^{-10} for the $4\,^1S$ and $5\,^1S$ excited states. [Extending the range of integration in view of (7) leads to a slight degrading of precision.] The largest error in (ii) comes from interpolating to find a zero of the determinant [24,25], defining the energy eigenvalue E. We have determined E usually to 8–10 significant figures, which is why most of our results appear with this accuracy. Of course, this could be improved, if necessary, to up to 12–13 significant figures by solving our equations with more trial energies to get a more accurate eigenvalue extrapolation. The precision of (iii) is about 10^{-10} except for $K_m=32$ where it is about 10^{-8} because

a less dense numerical quadrature is used. (The expectation value of the Hamiltonian $\langle H \rangle$ usually has 1–2 more figures accuracy than E or other expectation values because of its variational nature [3,6].)

The results of the calculations of eigenvalues E, of expectation values of the Hamiltonian $\langle H \rangle$, of different functions of interparticle distances, and of the absolute value of the local deviation $\langle |\Delta| \rangle$ (%) are given in Tables I–IV. The number of significant figures shown expresses the estimated numerical accuracy in each entry. The value of E in Table II for $K_m=48$ differs from that of Ref. [8] because we now use a more accurate extrapolation to the zero of the determinant from computations at different trial energies than we used previously. The difference of $\langle H \rangle$ values for $K_m=32,48$ in this table from those of Ref. [8] reflects this change and also a correction of a minor error in the program that calculates $\langle H \rangle$. (The correction does not affect any other expectation values to the indicated accuracy.) Finally, the $\langle |\Delta| \rangle$ values for the $2\,^1S$ state differ from those in Table VII of Ref. [8] because (i) we erroneously listed in Table VII of Ref. [8] averages of $(H\psi/\psi)-E$ instead of expectation values of $\Delta=(H\psi/E\psi)-1$; (ii) we now use a more dense integration quadrature.

As described in work [3], in the CFHH approach the eigenvalue of the effective Schrödinger equation E differs from the expectation value of the Hamiltonian $\langle H \rangle$ because, with a finite K_m, V' is non-Hermitian. They are both estimates of the energy, but approach each other only for infinite K_m, with $\langle H \rangle$ (not E) having the sta-

TABLE I. Calculated energy eigenvalue E and the expectation values of the Hamiltonian $\langle H \rangle$, of different functions of interparticle distances (a.u.) and of the absolute value of the local deviation $\langle |\Delta| \rangle$ (%) for the helium $2\,^1S$ excited state. The index 3 indicates the helium nucleus whose mass is presumed to be infinite. K_m is the maximum global angular momentum and N is the number of hyperspherical functions included. The number of digits indicates the numerical precision of calculated values. The correlation parameters $\gamma=2$, $\delta=-0.5$ correspond to the cusp parameterization used earlier in the CFFH ground-state helium calculations [3,4,6,8]. The last lines of the table contain the results of the precision CFHH calculations [4] with the uncorrelated cusp parametrization and of the most sophisticated variational computations [12–16].

K_m	N	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle \delta(\mathbf{r}_{12}) \rangle$	$\langle r_{12} \rangle$	$\langle r_{12}^{2} \rangle$
32	81	0.144 478 56	0.250 384 88	0.008 701 162 4	5.251 754 5	32.047 754
40	121	0.143 987 98	0.249 932 55	0.008 666 662	5.263 026 6	32.205 544
48	169	0.143 825 29	0.249 779 30	0.008 655 267 5	5.267 029 5	32.262 952
56	225	0.143 765 93	0.249 722 84	0.008 651 220 9	5.268 553 5	32.285 237
Ref. [4]		0.143 753 05	0.249 682 30	0.008 805 145 2	5.269 720 9	32.302 747
Ref. [28]		0.143 743	0.249 683 38	0.008 679	5.269 657 4	32.301 60
Ref. [12]				0.008 652 1	5.269 688	32.302 18
Ref. [13]				0.008 648 444 6		
Ref. [14]				0.008 65		
Ref. [16]				0.008 648 489 3		

K_m	N	$\langle r_{13}^{-2} \rangle$	$\langle r_{13}^{-1} \rangle$	$\langle \delta(\mathbf{r}_{13}) \rangle$	$\langle r_{13} \rangle$	$\langle r_{13}^{2} \rangle$
32	81	4.146 569 1	1.135 691 5	1.309 240 9	2.964 050 7	15.962 237
40	121	4.146 855 4	1.135 509 3	1.309 371 29	2.969 706 6	16.040 864
48	169	4.146 901 1	1.135 447 5	1.309 418 55	2.971 718 3	16.069 517
56	225	4.146 923 5	1.135 424 6	1.309 444 503	2.972 485 1	16.080 652
Ref. [4]		4.146 893 8	1.135 403 9	1.309 432 1	2.973 070 7	16.089 365
Ref. [28]		4.146 783	1.135 407 8	1.309 272	2.973 038 5	16.088 81
Ref. [12]				1.309 447	2.973 057	16.089 13
Refs. [13,16]				1.309 460 778		
Ref. [14]				1.309 46		

K_m	N	$\langle (r_{12}r_{13})^{-1} \rangle$	$\langle (r_{13}r_{23})^{-1} \rangle$	$\langle \lvert\Delta\rvert \rangle$	$-E$	$-\langle H \rangle$
32	81	0.341 810 50	0.563 607 09	0.106	2.145 732 78	2.145 970 98
40	121	0.341 049 64	0.562 481 38	0.061	2.145 899 427	2.145 973 54
48	169	0.340 793 98	0.562 100 76	0.041	2.145 948 244	2.145 973 88
56	225	0.340 700 08	0.561 960 81	0.027	2.145 964 507	2.145 974 02
Ref. [4]		0.340 632 78	0.561 859 16			2.145 973 851
Ref. [28]						2.145 973 824
Ref. [12]						2.145 973 30
Ref. [13,16]						2.145 974 046 05
Ref. [14]						2.145 974 046
Ref. [15]						2.145 974 045 82

TABLE II. Same as in Table I, but for the $3\,^1S$ excited state. The last lines of the table contain the results of the variational calculations [12,14–16].

K_m	N	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle\delta(\mathbf{r}_{12})\rangle$	$\langle r_{12}\rangle$	$\langle r_{12}^{2}\rangle$
32	81	0.041 592 655	0.112 732 57	0.002 497 444 9	12.199 279	169.011 32
40	121	0.041 260 291	0.112 333 90	0.002 474 434 9	12.227 928	169.707 97
48	169	0.041 013 389	0.112 013 64	0.002 457 682 2	12.255 723	170.452 17
56	225	0.040 860 234	0.111 808 61	0.002 447 382 2	12.274 844	170.982 21
Ref. [12]				0.002 5	12.305	171.9
Ref. [14]				0.002 43		
K_m	N	$\langle r_{13}^{-2}\rangle$	$\langle r_{13}^{-1}\rangle$	$\langle\delta(\mathbf{r}_{13})\rangle$	$\langle r_{13}\rangle$	$\langle r_{13}^{2}\rangle$
32	81	4.093 733 4	1.059 012 6	1.282 902 8	6.459 069 7	84.479 78
40	121	4.040 228 2	1.058 848 2	1.282 958 3	6.473 359 3	84.826 249
48	169	4.040 294 4	1.058 717 7	1.283 016 9	6.487 252 9	85.197 469
56	225	4.040 348 0	1.058 634 4	1.283 059 4	6.496 817 9	85.462 113
Ref. [12]				1.283 12	6.512	85.9
Ref. [14]				1.283 14		
K_m	N	$\langle (r_{12}r_{13})^{-1}\rangle$	$\langle (r_{13}r_{23})^{-1}\rangle$	$\langle\lvert\Delta\rvert\rangle$	$-E$	$-\langle H\rangle$
32	81	0.138 940 42	0.243 167 64	0.080	2.060 573 97	2.061 265 653
40	121	0.138 331 38	0.242 219 70	0.053	2.060 901 68	2.061 268 874
48	169	0.137 855 26	0.241 468 75	0.035	2.061 082 66	2.061 270 727
56	225	0.137 553 61	0.240 990 48	0.023	2.061 174 79	2.061 271 511
Ref. [12]						2.061 270 53
Ref. [15]						2.061 271 989 33
Ref. [16]						2.061 271 989 74

TABLE III. Same as in Table I, but for the $4\,^1S$ excited state.

K_m	N	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle\delta(\mathbf{r}_{12})\rangle$	$\langle r_{12}\rangle$	$\langle r_{12}^{2}\rangle$
32	81	0.018 3	0.065 5	0.001 11	21.75	533
40	121	0.017 268 175	0.063 581 328	0.001 035 920 0	22.255 768	558.731 4
48	169	0.017 015 268	0.063 230 140	0.001 018 984 3	22.292 932	559.796 59
56	225	0.016 890 482	0.063 052 277	0.001 010 647 2	22.314 537	560.494 28
Ref. [12]				0.001	22.37	563
Ref. [14]				0.000 999		
K_m	N	$\langle r_{13}^{-2}\rangle$	$\langle r_{13}^{-1}\rangle$	$\langle\delta(\mathbf{r}_{13})\rangle$	$\langle r_{13}\rangle$	$\langle r_{13}^{2}\rangle$
32	81	3.476	1.033 9	1.277 7	11.25	267
40	121	4.017 126 4	1.032 947 6	1.277 435 8	11.494 203	279.342 5
48	169	4.016 815 0	1.032 745 6	1.277 350 8	11.512 855	279.880 94
56	225	4.016 656 6	1.032 643 1	1.277 307 0	11.523 691	280 230 06
Ref. [12]				1.277 2	11.55	281.5
Ref. [14]				1.277 27		
K_m	N	$\langle (r_{12}r_{13})^{-1}\rangle$	$\langle (r_{13}r_{23})^{-1}\rangle$	$\langle\lvert\Delta\rvert\rangle$	$-E$	$-\langle H\rangle$
32	81	0.077 0	0.138 8	0.04	2.033 630 75	2.033 491
40	121	0.074 454 733	0.134 478 78	0.026	2.033 618 690	2.033 587 81
48	169	0.073 940 508	0.133 656 78	0.017	2.033 573 548	2.033 586 664
56	225	0.073 682 267	0.133 242 21	0.012	2.033 563 310	2.033 586 584
Ref. [12]						2.033 584 70
Ref. [15]						2.033 586 728
Ref. [16]						2.033 586 717 02

TABLE IV. Same as in Table I, but for the $5\,^1S$ excited state.

K_m	N	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle\delta(\mathbf{r}_{12})\rangle$	$\langle r_{12}\rangle$	$\langle r_{12}^{2}\rangle$
32	81	0.013 1	0.050	0.000 81	29.8	1006
40	121	0.008 4	0.040	0.000 52	35	1400
48	169	0.008 66	0.040 56	0.000 519	35.4	1410
56	225	0.008 598 561	0.040 501 280	0.000 514 714 67	35.336 08	1400.973
Ref. [12]				0.001	35.5	1408.0
Ref. [14]				0.000 502		

K_m	N	$\langle r_{13}^{-2}\rangle$	$\langle r_{13}^{-1}\rangle$	$\langle\delta(\mathbf{r}_{13})\rangle$	$\langle r_{13}\rangle$	$\langle r_{13}^{2}\rangle$
32	81	4.013	1.026	1.267 8	15.2	503
40	121	4.009	1.021	1.275 4	18.0	700
48	169	4.008 63	1.020 87	1.275 37	18.06	705
56	225	4.008 543 6	1.020 8277	1.275 353 4	18.037 593	700.473 6
Ref. [12]				1.275 2	18.10	704.0
Ref. [14]				1.275 261		

K_m	N	$\langle (r_{12}r_{13})^{-1}\rangle$	$\langle (r_{12}r_{23})^{-1}\rangle$	$\langle\lvert\Delta\rvert\rangle$	$-E$	$-\langle H\rangle$
32	81	0.058 6	0.016	0.09	2.019 988 59	2.019 99
40	121	0.046	0.084	0.023	2.021 402 39	2.021 25
48	169	0.046 0	0.084 7	0.016	2.021 290 37	2.021 184
56	225	0.045 910 700	0.084 687 05	0.013	2.021 249 57	2.021 164 9
Ref. [12]						2.021 175 22
Ref. [14]						2.021 176 851 3
Ref. [15]						2.021 176 783 7
Ref. [16]						2.021 176 851 57

tionarity property. One has, however, to keep in mind that for the nth excited state $\langle H\rangle$ does not provide an upper bound of energy, since

$$\langle\psi|H|\psi\rangle-E_n=\sum_{m\ (\neq n)}|c_m|^2(E_m-E_n) \tag{8}$$

where

$$\psi=\sum_m c_m\psi_m,\quad \sum_m|c_m|^2=1\ ,$$

where ψ_m and E_m are exact wave functions and energies of excited states. From (8) even a small admixture of lower excited states for which $E_m-E_n<0$ could make the expectation value $\langle\psi|H|\psi\rangle$ of the Hamiltonian more attractive than E_n, as indeed happens in the cases of the $4\,^1S$ ($K_m=40$) and $5\,^1S$ ($K_m=40,48$) excited states (see Tables III and IV).

Some of the expectation values in Tables II–IV appear with less significant figures than others (e.g., r_{12} for $K_m=32$ in Table III). The failure to be able to express these quantities more accurately has to do with a difficulty in computing asymptotic wave functions. To discuss this problem, we note that the coupled differential equations in the CFHH method [2–8] in the limit $\rho\to\infty$ have a form [24,25]

$$\left[-\frac{\partial^2}{\partial\rho^2}+D\frac{\partial}{\partial\rho}+W-2E\right]\phi=0\ , \tag{9}$$

where D and W are $N\times N$ matrices (depending on the correlation parameters), ϕ is a vector of dimension N, and $N=[(K_m/4)+1]^2$ is the number of the equations. For simplicity, we will discuss the simplest case of $K_m=0$ ($N=1$) but all features are extendable to higher K_m. In this instance the asymptotic solution of (9) is

$$\phi=C_+e^{\kappa_+\rho}+C_-e^{\kappa_-\rho},\quad \kappa_\pm=\frac{D\pm[D^2+4(W-2E)]^{1/2}}{2}\ . \tag{10}$$

If $\kappa_\pm$ are real, then the physical solution corresponds to $C_+=0$, which is the solution we propagate [6]. The asymptotic form of the wave function in view of (1) and (3) therefore is

$$\psi\to\exp\{[-\gamma(R_{13}+R_{23})-\delta R_{12}+\kappa_-]\rho\}\ , \tag{11}$$

where $R_{ij}=r_{ij}/\rho$. For ψ to be square integrable, the argument in (11) must be negative for all possible R_{ij}. For the infinite mass M and cusp parameters $\gamma=2$, $\delta=-0.5$, the least slow decay occurs when r_{13} (r_{23}) approaches infinity and r_{23} (r_{13}) is finite, in which case

$$\psi\to\exp[(-\gamma-\delta+\kappa_-)\rho]\equiv\exp[(-1.5+\kappa_-)\rho]\ . \tag{12}$$

While in the limit of infinitely large K_m the wave function ψ approaches the exact wave function and is hence square integrable, this does not necessarily guarantee that κ_-, when determined by a finite truncation of the full set of equations, is such that ψ decays exponentially over the

full configuration space. Indeed, we find often for lower K_m, as in the case $K_m=32$ for $3\,^1S$, that in the configuration $r_{23}\gg r_{13}$ (or $r_{13}\gg r_{23}$) the wave function is well behaved and converged for small and moderate ρ, but eventually for very large ρ an exponentially increasing behavior in the wave function starts to dominate. In the cited example the wave function is well behaved and decaying for $\rho<60$ a.u. For larger ρ the exponentially increasing behavior takes over in the configurations $r_{23}\gg r_{13}$ (or $r_{13}\gg r_{23}$), causing the nonconvergence of integrals used for operator averages. If the convergence of these integrals is viewed as a function of ρ_c, a cutoff hyperradius past which the wave function is (artificially) set to zero, the behavior appears convergent as long as ρ_c has small or moderate values, but eventually the exponentially increasing part leads to divergent behavior for very large ρ_c. At a certain ρ_c each average has the most stable value (with respect to changes in ρ_c), indicating the smallest overall magnitude of the wave function, and these are the values given in the tables, with the number of significant figures kept indicating the stability. Fortunately, as K_m increases, the stability increases and the problem disappears (e.g., for $3\,^1S$ the $K_m=48$ wave function decays for all ρ for $r_{23}\gg r_{13}$ or $r_{13}\gg r_{23}$).

The asymptotic behavior provides another reason why $\langle\psi|H|\psi\rangle$ may indicate more binding than the exact energy. With a boundary at $\rho=\rho_c$, and $\psi=\psi_n+\delta\psi$, where ψ_n is the exact wave function, one has, in view of $H=-\frac{1}{2}\nabla^2+V$,

$$\langle\psi|H|\psi\rangle-E_n=\langle\delta\psi|H|\delta\psi\rangle+\tfrac{1}{2}\int(\delta\psi\nabla\psi-\psi\nabla\delta\psi)d\mathbf{s}\ , \tag{13}$$

where $\int d\mathbf{s}$ indicate integration over the hyperspherical surface at $\rho=\rho_c$. The last term in (13) could be negative thus counteracting the Rayleigh-Ritz principle. Again, this effect disappears with large K_m, but it does show up in some of our calculated values of $\langle H\rangle$ (e.g., $4\,^1S$, $K_m=40$). Finally, one can decrease this problem by choosing the δ parameter to minimize or eliminate the exponential increase in (11), but at the cost of sacrificing the correct electron-electron cusp behavior. This is, in fact, the approach used in the "uncorrelated cusp" and "asymptotic cusp" parametrizations for different systems in Refs. [4,5,8] and Ref. [7], respectively.

Our results clearly illustrate that even with the simplest choice of the correlation factor (3) the CFHH method works very well for excited states. Indeed, comparison of our results for $K_m=48$ and 56 shows that the precision of our calculations converges for the expectation values of the Hamiltonian up to an error in about the eighth significant figure and for other expectation values up to an error in about the fifth significant figure. The results for the averages of the absolute value of the local deviation $\langle|\Delta|\rangle$ indicate that the quality of wave functions is very high. Values presented here are better than those obtained in variational calculations of Accad, Pekeris, and Schiff [12] with the Hylleraas-type variational wave functions and in generator coordinate computations of Thakkar and Smith [28]. Even with our choice of the very simple correlation factor (3), our results agree well with the most sophisticated variational calculations of Drake [13] and Kono and Hattori [14], who use trial functions, constructed with two groups of basis functions. They also agree well with the results of Frankowsky [15] and Baker, Hill, and Morgan [16], whose basis functions incorporate logarithmic terms. Both modifications of the Hylleraas expansion yield more rapidly convergent variational energies.

Improvements in the correlation function used in the current calculation are nevertheless desirable. One cannot simultaneously build in both a satisfactory asymptotic and cusp behavior with the symmetric linear correlation factor f we have chosen. As a result the present calculation (see also Ref. [8]) of the $2\,^1S$ state with the cusp parametrization yields better short-distance behavior and the previous calculation [4,8] with the so-called uncorrelated cusp parametrization [2–8] (better adjusted to a description of asymptotic behavior) produces somewhat better results for large distances (compare Table I with Table III of Ref. [4]). The quality of a wave function and accuracy of the calculated energies in both computations are comparable. For example, as one can see from Table I, the convergence of expectation values of operator $\delta(\mathbf{r}_{12})$, which stresses very small electron-electron distances, in the present cusp parametrization is significantly better than in the correlated cusp parametrization [4], while the convergence of expectation values of r_{12}^2, defined by large electron-electron distances, is worse.

Including both cusp and asymptotic behavior becomes especially important for higher excitations where particles spend more time apart from each other. This also would alleviate the discussed difficulty in extracting the asymptotic wave function. The inability of the current correlation factor (3) to include the asymptotic behavior leads to slower convergence of certain expectation values and lower quality of wave functions (higher values of the local deviation Δ) for large interparticle distances [8]. Therefore for very highly excited states one should consider more general nonsymmetric nonlinear correlation functions that can properly describe both cusp and asymptotic behavior [2,8]. That will allow very precise estimates of highly excited state wave functions both at small and large interparticle distances where their exact knowledge is imperative for an accurate calculation of the relativistic, QED, and finite-nuclear-size effects [13,14,16] as well as dipole matrix elements necessary, for example, for detecting parity violation in the helium atom [26]. However, as the present and previous [3,4,6,8] calculations of the helium atom with the CFHH method show, for the first few excited states even the simplest correlation factor (3) is satisfactory. Moreover, the choice of the simplest correlation factor (3) with "cusp" parametrization gives a surprisingly accurate description of the wave functions demonstrating the power of the CFHH method for excited states. Therefore even the simple CFHH approach can be used, for example, in a very accurate calculation of the two-electron helium Lamb shifts. These Lamb shifts were recently measured

very precisely for different excited states and their values [27] show large deviation (equal to about 5–20 experimental uncertainty ranges) from theoretical predictions, obtained in the most sophisticated variational calculations. Work along these lines is presently in progress as well as employing the more sophisticated correlation functions.

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[1] R. Jastrow, Phys. Rev. **98**, 1479 (1955).
[2] V. B. Mandelzweig, Nucl. Phys. **A508**, 63c (1990).
[3] M. I. Haftel and V. B. Mandelzweig, Phys. Lett. A **120**, 232 (1987).
[4] M. I. Haftel and V. B. Mandelzweig, Phys. Rev. A **38**, 5995 (1988).
[5] M. I. Haftel and V. B. Mandelzweig, Phys. Rev. A **39**, 2813 (1989).
[6] M. I. Haftel and V. B. Mandelzweig, Ann. Phys. (N.Y.) **189**, 29 (1989); **195**, 420 (1989).
[7] M. I. Haftel and V. B. Mandelzweig, Phys. Rev. A **41**, 2339 (1990).
[8] M. I. Haftel and V. B. Mandelzweig, Phys. Rev. A **42**, 6324 (1990).
[9] D. E. Freund, B. D. Huxtable, and J. D. Morgan, Phys. Rev. A **29**, 980 (1984).
[10] D. Ceperley and B. J. Adler, Phys. Rev. A **31**, 1999 (1985).
[11] J. H. Bartlett, J. J. Gibson, and C. G. Dunn, Phys. Rev. **47**, 679 (1935).
[12] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971); C. L. Pekeris, Phys. Rev. **115**, 1216 (1959); **126**, 143 (1962); **126**, 1470 (1962); **127**, 509 (1962).
[13] G. W. F. Drake, Nucl. Instrum. Methods B **31**, 7 (1988).
[14] A. Kono and S. Hattori, Phys. Rev. A **34**, 1728 (1986).
[15] K. Frankowsky, Phys. Rev. **160**, 1 (1967).
[16] J. Baker, R. N. Hill, and J. D. Morgan III, in *Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms,* Proceedings of the Program held on Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms at the Institute of Theoretical Physics, Santa Barbara, CA, 1988, AIP Conf. Proc. No. 189, edited by W. Johnson, P. Mohr, and J. Sucher (AIP, New York, 1988), p. 123; J. D. Morgan III (private communication).
[17] V. B. Mandelzweig, Phys. Lett. **80A**, 361 (1980); **82A**, 471 (1981).
[18] N. Barnea and V. B. Mandelzweig, Phys. Rev. A **41**, 5209 (1990).
[19] N. Barnea and V. B. Mandelzweig, this issue, Phys. Rev. A **44**, 7053 (1991).
[20] R. Krivec and V. B. Mandelzweig, Phys. Rev. A **42**, 3779 (1990).
[21] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1962), Vol. 1.
[22] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1980).
[23] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[24] V. B. Mandelzweig, Phys. Lett. **78A**, 25 (1980).
[25] M. I. Haftel and V. B. Mandelzweig, Ann. Phys. (N.Y.) **150**, 48 (1983).
[26] G. v. Oppen, Europhys. Lett. **11**, 25 (1990).
[27] C. J. Sansonetti, J. D. Gillaspy, and C. L. Cromer, Phys. Rev. Lett. **65**, 2539 (1990).
[28] A. J. Thakkar and V. H. Smith, Phys. Rev. A **15**, 16 (1977).