Precise nonvariational calculations on the helium atom

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The Schrödinger equation is solved directly for the ground state and excited $2\,^1S$ state of the helium atom by using a rapidly convergent hyperspherical method which involves no adjustable parameters. The double and triple coalescence points are taken into account analytically. The center-of-mass motion is treated nonperturbatively, and the cases of infinite and finite nuclear masses are considered. The inclusion of 169 hyperspherical functions yields the precision of a few parts in 10^9 and 10^8 for the expectation value of the Hamiltonian operator and for all other expectation values, respectively, for the ground state, with only slightly less accuracy for the excited state.

During the last 60 years the two-electron atoms have been the subject of extensive variational calculations.[1-9] Though a precision of the calculated energies is now better[8,9] than a few parts in 10^{13}, a few problems still remain. First, different algorithms for selecting the basis functions lead to variational wave functions that are differently tailored to describe electron correlations. For example, the Freund-Huxtable-Morgan (FHM) basis,[9] which includes many functions with high powers of u/s, does a better job of describing short- and moderate-range electron correlations than the Frankowski-Pekeris (FP) basis.[8] The latter basis contains high powers of s and is better adjusted for the proper description of long-range correlations. (Here s and u are the Hylleraas coordinates, $s=r_1+r_2$ and $u=r_{12}$). While the accuracy of the calculated energies is extremely good in both cases, the FHM and FP descriptions of the exponentially decreasing tail of the wave function, which makes very little contribution to the energy, tend to be rather different. Similarly, the inclusion or omission of the logarithmic terms predicted by Bartlett[10] and Fock,[11] while making little effect on the variational energy[8,9] (changing it only by a few parts in 10^{12}), leads to a completely different analytic structure of the variational wave function. Thus an approximate wave function that gives an accurate variational energy value can have relatively different analytic structure than the exact solution of the Schrödinger equation. Since variational wave functions are conditioned to give a minimum of the expectation value of the Hamiltonian, they only have to resemble the exact wave function "on the average", and not locally.[12] They therefore can yield, in principle, rather poor expectation values of different operators, especially those which have a significant contribution from the specific region of the wave function. For example, inverse-square and δ function operators depend on the wave function at the small interparticle separations, while the dipole and quadrupole moment operators have major contributions from the tail region. These are exactly the operators whose expecta-

tion values determine the relativistic and hyperfine corrections,[6] positron annihilation, and parity violation in atoms.[13-15]

The general belief that such a problem can always be overcome by saturating the basis with additional functions has been proved to be false. For example, the expectation values of operators u^n, $n>0$, obtained from a "good" variational wave function (i.e., one that gives a very accurate binding energy) may converge to a wrong limit or even diverge.[16]

Modern experiments, such as recent high-order precision measurements of transition energies in helium and heliumlike ions,[17] are sensitive not only to relativistic and quantum electrodynamical effects, but also to the analytic and clustering structure of the wave function. To obtain accurate wave functions, several attempts of numerical solution of the Schrödinger equation for two-electron atoms have been considered. In Refs. 18 and 19 the finite-difference and finite-element methods were used, while in Ref. 20 the hyperspherical-coordinates method was employed. The ground-state energy of the helium atom was accurate to a few parts in 10^4 and 10^6, respectively. The error in the other expectation values, which, unlike the expectation value of the Hamiltonian, is generally proportional to the error in the wave function to the first power, was a few parts in 10^2 or 10^3. This falls far behind the accuracy of modern variational calculations.[8,9]

Recently, however, a very efficient method of direct solution of the three-body Schrödinger equation, which uses no adjustable parameters, was introduced.[21] The method is based on a decomposition of a wave function ψ into a product of a correlation factor χ, describing the singular and/or cluster structure, and a smooth factor ϕ, which is expanded in a rapidly absolutely and uniformly convergent series of hyperspherical harmonic functions. This technique possesses, besides its extreme precision and generality, some other very attractive features. Since hyperspherical coordinates are used (which allow a sepa-

ration of the center-of-mass motion), the method is equally applicable not only to three-body atomic systems, but also to mesic molecules consisting of three particles of comparable masses and to systems of two heavy and one light particles, such as H_2^+. Excited-state wave functions, being solutions of the same equation with different eigenvalues, are automatically orthogonal to the ground state or to each other. In the present paper we present precise calculations for the expectation values of the Hamiltonian and other operators for the helium ground state using this method.

In the center-of-mass frame ϕ satisfies the three-body six-dimensional Schrödinger equation with an effective velocity dependent potential.[21] To make ϕ as smooth as possible, we have chosen,[21] for the helium ground state, $\chi = \exp[-2(r_{13} + r_{23} - r_{12}/4)]$ to incorporate the singularities at $r_{ij} = 0$, i.e., the cusps in the wave function. In that case the effective potential contains no singularities, which facilitate a faster convergence[21] of the hyperspherical expansion.

The numerical technique of the present calculations is the same as in Ref. 21. The numerical precision is increased to an estimated error of about one part in 10^{13} in the integration of 169 coupled radial differential equations needed for an evaluation of a wave function for maximal global quantum number $K_m = 48$. To integrate the 169 coupled equations for $K_m = 48$ to 12 or 13 significant figure precision required about 45 min of CPU time on the Naval Research Laboratory's CRAY-XMP computer. Since the precision obtained was much more than needed and since no special effort was made to vectorize the code, we estimate that one should be able to reduce this CPU time by about an order of magnitude. The numerical integrals involved in the calculation of expectation values of the Hamiltonian and of other operators are carried out to an estimated error of a few parts in 10^{11} and 10^9, respectively.

The results for ground state of the helium atom in the case of infinite and finite nuclear masses are presented in Tables I and II. While the detailed discussion of the convergence patterns will be given elsewhere, a simple look at the tables shows that the precision of the expectation values of the Hamiltonian is one part in 10^9 and the accuracy of all other expectation values is seven or eight significant figures. The agreement with the best variational calculations[6–9,22,23] is excellent. There are only slight disagreements in the $1/r_{12}$ and r_{12} expectation values, with our values better converged than those of Pekeris[6] with 1078 basis functions. These expectation values are especially sensitive to the wave function near the cusps. The discrepancy thus reflects the fact that the coefficients before r_{12} in the expansion of the variational wave function at the origin is reproduced with a gross deviation of 5% from its true value,[6] even though the corresponding variational energy has an inaccuracy of one part in 10^{10}.

With regard to the energies for a finite-mass nucleus, our value is within 2×10^{-7} a.u. of the value obtained by Pekeris[6] in first-order perturbation theory. A simple estimate shows that second-order corrections should be of the order of 6×10^{-8} a.u. which is consistent with the

difference between Pekeris's value and ours. Since in our method center-of-mass motion is taken into account nonperturbatively, the finite-mass entries for all expectation values in Tables I and II are exact with respect to finite-mass effects. To our knowledge these are the first precise nonperturbative determinations of most of these expectation values for a helium atom with finite nuclear mass. Inclusion of finite-mass corrections for certain relativistic operators have recently been reported by J. D. Morgan III and J. Baker[22] and by G. W. F. Drake.[23] Tables I and II show excellent agreement between our expectation values and those of Morgan[22] for Hamiltonian and δ-function operators for a finite-mass nucleus. In view of the fact that the accuracy of the experimental energies reaches nine digits, this effect is very important for correct estimates of the QED contributions and the precise determination of the Rydberg constant.

The proposed method also works well for excited states, as exhibited in the energy and expectation values (Tables I and III) for the excited 2^1S state of helium (with infinite nuclear mass). In this case we have chosen a correlation function $\chi = \exp[-2(r_{13} + r_{23})]$. This form incorporates the nucleus-electron cusps, but not the electron-electron cusp. This form does imply uncorrelated electron-electron motion, which is, in fact, what we would expect for an atom whose dominant configuration is $1s2s$. A parameterization including the e-e cusp is not as accurate for this state as it poorly describes the large-

TABLE I. The expectation values $\langle H \rangle$ of the Hamiltonian (a.u.). K_m is the maximum global angular momentum involved and N is the number of hyperspherical functions included and equations solved. The number of digits indicate the numerical precision of the calculated value. The two numbers for the ground state (GS) are for infinite and finite ($M_e/M_{\text{nucleus}} = 1.3709337 \times 10^{-4}$) nuclear masses, respectively. The reference rows display the results of the most sophisticated variational calculations (Refs. 6, 8, 9, and 22).

K_m	N	$-\langle H \rangle$ He (GS)	He* (2^1S)
0	1	2.855 504 862	2.004 280 769
		2.855 030 357	
8	9	2.903 701 425	2.145 297 956
		2.903 281 569	
16	25	2.903 723 654	2.145 968 877
		2.903 303 834	
24	49	2.903 724 254	2.145 972 605
		2.903 304 434	
32	81	2.903 724 340	2.145 973 445
		2.903 304 520	
40	121	2.903 724 361	2.145 973 760
		2.903 304 542	
48	169	2.903 724 368	2.145 973 851
		2.903 3045 549	
Refs. 8 and 9		2.903 724 377	
Ref. 6		2.903 304 374	
Ref. 22		2.903 724 377	2.145 974 046
		2.903 304 558	

distance uncorrelated behavior. The price we pay for not including the e-e cusp shows up mainly in a slower convergence rate for the average of singular functions of r_{12} [especially $\langle \delta(\mathbf{r}_{12}) \rangle$]. As for a system with comparable masses, preliminary calculations for Ps$^-$ also indicate a vast improvement over the unmodified hyperspherical method. Using a simple parameterization χ $= \exp[-0.362(r_{13}+r_{23})]$, which implies uncorrelated e^--e^- motion with a symmetric disposition of the electrons asymptotically, values of $-\langle H \rangle$ of 0.2589, 0.2603, 0.2609, and 0.2613 a.u. are obtained for $K_m = 8$, 12, 16, and 20, respectively. This compares with 0.2423, 0.2505, 0.2543, and 0.2567 a.u. for the usual hyperspherical-harmonic method,[24] and the "exact" result of 0.262 005 a.u.[25] An uncorrelated-cusp parameterization, as used in

He*, yields an excellent eigenvalue[21] of 0.2621 a.u. for $K_m = 20$, but yields a wave function with an unsatisfactory asymptotic form. Whether a simple form of χ can be found to yield accuracies comparable to the helium atom is now under investigation. With the accuracies exhibited so far, it appears likely that this technique could be quite efficient in the three- or four-nucleon problem as well as in calculations of the wave function of muonic molecular ions (like μ-d-t) of interest in muon-catalyzed-fusion research.[26,27]

Summing up, we have presented a method of solution of the three-body Schrödinger equation that allows precise direct calculation of the wave function. The dependence of the wave function on the hyperspherical radius, which equals zero at the triple coalescence point, is given

TABLE II. Expectation values of various functions of r_{12} and r_{13}, the distances between two electrons, and an electron and the nucleus, for the helium ground state. The number of digits indicate the numerical precision of the calculated value. The two numbers in each entry of the table are for infinite and finite nuclear masses, respectively. The reference rows display the results of the most precise variational calculations (Refs. 6, 22, and 23).

K_m	N	r_{12}^{-2}	r_{12}^{-1}	$\delta(\mathbf{r}_{12})$	r_{12}	r_{12}^2	$(r_{12}r_{23})^{-1}$
0	1	1.307 338	0.894 495 4	0.088 703 33	1.501 529 0	2.801 223 2	1.816 513 7
		1.306 833	0.894 325 8	0.088 648 60	1.501 809 9	2.802 267 3	1.1815 868 3
8	9	1.466 392	0.946 555 1	0.106 389 19	1.420 245 5	2.508 254 8	1.922 847 0
		1.466 009	0.946 435 0	0.106 344 01	1.420 419 7	2.508 862 5	1.922 311 8
16	25	1.464 833 9	0.945 852 97	0.106 331 263	1.422 197 71	2.515 992 87	1.921 033 63
		1.464 445 5	0.945 731 80	0.106 285 866	1.422 154 13	2.516 614 38	1.920 495 97
24	49	1.464 771 9	0.945 820 99	0.106 338 556	1.422 206 25	2.516 399 52	1.920 950 66
		1.464 385 6	0.945 699 76	0.106 293 146	1.422 239 78	2.517 021 96	1.920 412 87
32	81	1.464 769 2	0.945 818 50	0.106 342 037	1.422 069 80	2.516 436 11	1.920 944 12
		1.464 384 1	0.945 697 60	0.106 297 170	1.422 246 42	2.517 056 26	1.920 407 90
40	121	1.464 769 84	0.945 818 335	0.106 343 557 5	1.422 070 472	2.516 439 988	1.920 943 657
		1.464 383 52	0.945 697 049	0.106 298 137 2	1.422 247 739	2.517 062 533	1.920 405 835
48	169	1.464 770 31	0.945 818 369	0.106 344 284 7	1.422 070 455	2.516 440 118	1.920 943 726
		1.464 384 01	0.945 697 143	0.106 298 870 5	1.422 247 714	2.157 062 655	1.920 405 929
Ref. 6		1.464 773	0.945 818 451	0.106 355	1.422 070 26	2.516 439 34	1.920 944
Ref. 22				0.106 345 332 9			
				0.106 299 919			
Ref. 23				0.106 345 380			

K_m	N	r_{13}^{-2}	r_{13}^{-1}	$\delta(\mathbf{r}_{13})$	r_{13}	r_{13}^2	$(r_{13}r_{23})^{-1}$
0	1	5.718 65	1.651 376	1.682 077 9	0.937 691 1	1.196 674 3	2.642 202
		5.716 77	1.651 097	1.681 270 8	0.937 854 8	1.197 095 8	2.641 296
8	9	6.017 76	1.688 759	1.809 798 9	0.928 530 0	1.189 700 1	2.711 157
		6.016 08	1.688 519	1.809 043 6	0.928 663 9	1.190 044 5	2.710 372
16	25	6.017 352	1.688 337 0	1.810 294 34	0.929 417 88	1.193 247 78	2.708 782 0
		6.015 610	1.688 096 9	1.809 537 90	0.929 553 39	1.193 599 14	2.707 993 4
24	49	6.017 391	1.688 318 4	1.810 390 23	0.929 466 89	1.193 458 25	2.708 666 6
		6.015 700	1.688 078 3	1.809 633 58	0.929 602 50	1.193 810 09	2.707 877 8
32	81	6.017 403	1.688 316 9	1.810 413 79	0.929 471 66	1.193 479 73	2.708 656 4
		6.015 731	1.688 077 8	1.809 654 82	0.929 606 88	1.193 830 50	2.707 870 2
40	121	6.017 407 1	1.688 316 81	1.810 421 74	0.929 472 267	1.193 482 70	2.708 655 40
		6.015 715 1	1.688 076 58	1.809 664 91	0.929 607 889	1.193 834 59	2.707 866 57
48	169	6.017 408 2	1.688 316 81	1.810 425 06	0.929 472 341	1.193 483 12	2.708 655 34
		6.015 716 3	1.688 076 59	1.809 668 23	0.929 607 962	1.193 835 02	2.707 866 55
Ref. 6		6.017 407 1	1.688 316 80	1.810 419	0.929 472 297	1.193 483 01	2.708 656
Ref. 22				1.810 429 28			
				1.809 672 40			
Ref. 23				1.810 429 32			

TABLE III. Expectation values of various functions of r_{12} and r_{13} for the 2^1S excited state of helium. The notation is the same as Table II.

K_m	N	r_{12}^{-2}	r_{12}^{-1}	$\delta(r_{12})$	r_{12}	r_{12}^2	$(r_{12}r_{23})^{-1}$
0	1	0.373 062 3	0.395 662 6	0.033 497 05	3.532 349	14.684 47	0.545 363 8
8	9	0.158 237 2	0.261 840 7	0.010 473 47	4.997 002	28.691 76	0.361 691 3
16	25	0.143 841 47	0.249 613 05	0.009 066 363 6	5.270 696 3	32.308 53 0	0.340 486 58
24	49	0.143 799 47	0.249 657 27	0.008 943 849 1	5.270 390 2	32.311 782	0.340 583 81
32	81	0.143 779 46	0.249 676 91	0.008 876 879 9	5.269 888 8	32.305 096	0.340 621 62
40	121	0.143 763 55	0.249 681 21	0.008 834 374 4	5.269 759 9	32.303 307	0.340 630 35
48	169	0.143 753 05	0.249 682 30	0.008 805 145 2	5.269 720 9	32.302 747	0.340 632 78
Ref. 6				0.008 652 1	5.269 688	32.302 18	
Ref. 22				0.008 648 489 3			
Ref. 23				0.008 648 445 5			

K_m	N	r_{13}^{-2}	r_{13}^{-1}	$\delta(r_{13})$	r_{13}	r_{13}^2	$(r_{13}r_{23})^{-1}$
0	1	3.153 936	1.022 048	0.934 676 4	2.185 225	7.342 236	0.799 100 1
8	9	4.151 819	1.141 252	1.309 388 6	2.833 894	14.264 444	0.592 954 3
16	25	4.145 744 9	1.135 260 4	1.308 999 2	2.973 411 8	16.089 861	0.561 638 91
24	49	4.146 364 8	1.135 353 7	1.309 266 0	2.973 372 8	16.093 275	0.561 782 30
32	81	4.146 589 9	1.135 388 1	1.309 368 6	2.973 144 5	16.090 348	0.561 840 90
40	121	4.146 855 8	1.135 399 5	1.309 412 2	2.973 087 4	16.089 591	0.561 855 03
48	169	4.146 893 8	1.135 403 9	1.309 432 1	2.973 070 7	16.089 365	0.561 859 16
Ref. 6				1.309 447	2.973 057	16.089 13	
Ref. 22				1.309 460 8			
Ref. 23				1.309 460 8			

analytically by the logarithmic-power-series expansions[24,28] resulting from the exact solution of the Schrödinger equation. Therefore the logarithmic terms predicted by Bartlett[10] and Fock[11] are included automatically and exactly and so is the triple coalescence point. The double coalescence points are incorporated into a wave function analytically as well[21] through the correlation factor χ. As demonstrated here on for the helium ground state, the energies and other expectation values calculated with this wave function have the accuracy available earlier only in very elaborate variational calculations[6–9] involving hundreds or even thousands of variational parameters. A truncated wave function in our method converges to a true solution at every point in absolute and uniform fashion,[24,25] which enforces a similar convergence for expectation values. These features generally are not present in variational approaches, where the wave function is geared to facilitate the convergence of the expectation value of the Hamiltonian. In that case the correct behavior of the wave function at points that contribute little to the binding energy (such as points in the cusp or tail regions), as well as the convergence of expectation values of non-Hamiltonian operators, is not assured. Finally, the results for $He^*(2^1S)$ indicate that this method is capable of handling excited states accurately as well.

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