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Lowest-order relativistic corrections of helium computed using Monte Carlo methods

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We have calculated the lowest-order relativistic effects for the three lowest states of the helium atom with symmetry ^1S, ^1P, ^1D, ^3S, ^3P, and ^3D using variational Monte Carlo methods and compact, explicitly correlated trial wave functions. Our values are in good agreement with the best results in the literature.

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I. INTRODUCTION

When comparing theoretical atomic energies with their experimental counterparts, the nonrelativistic Schrödinger equation must be evaluated to high accuracy and a number of corrections must also be computed. Starting with the work of Hylleraas in the 1920s, explicitly correlated wave functions have been used to determine the nonrelativistic energies, the relativistic corrections (both lowest and higher order), the mass related corrections, and some QED corrections for helium [1–19] and lithium [20–34] to an accuracy that meets or exceeds the current level of experimental precision. This excellent agreement between theory and experiment is not yet true for the other atoms. The form of choice for two- and three-electron atoms, appropriately known today as a Hylleraas wave function, cannot be used for beryllium or any larger atom because it is difficult to analytically evaluate all the integrals needed to compute the energy. As a result, these systems have been examined using a number of other methods whose convergence is noticeably slower [35–49]. In the past decade Monte Carlo methods have been used to calculate a number of atomic energies to high accuracy. For smaller atoms (helium, lithium, beryllium) Monte Carlo methods are not as accurate as other explicitly correlated calculations but for larger atoms they are much more competitive and have recovered 99% of the correlation energy with a relatively compact wave function [50–54]. Because all integrals are computed numerically, this method has also been used to determine a variety of properties [55–62] including the relativistic corrections for several singlet S states [63–65]. Our ultimate goal is to use these Monte Carlo wave functions to calculate the relativistic corrections for a number of atoms. Before we can do so, however, we need to verify that this method can accurately evaluate these corrections for wave functions with high angular momenta. In this article we examine whether variational Monte Carlo techniques can accurately evaluate the lowest-order relativistic corrections and the mass polarization term for the three lowest states of helium with symmetry ^1S, ^1P, ^1D, ^3S, ^3P, and ^3D. Our goal is to compare the accuracy that we can get from a set of medium-quality, explicitly correlated wave functions with those from a high-quality Hylleraas wave function. In Sec. II we describe our trial wave function forms and determine the energy for each of our 18 states. Next, we use these wave functions to calculate the spin-independent terms. This work is described in Sec. III. In Sec. IV we first derive a detailed formula for each spin-dependent term and then we evaluate it. Finally, in Sec. V we calculate the singlet-triplet mixing for each state. This correction occurs because the spin-orbit operator causes a small mixing to take place between the singlet and the triplet wave functions. As a result, both the singlet and the triplet energies are slightly shifted. Unless otherwise indicated, all values in this article are given in atomic units and all calculations were performed with the 2006 CODATA values $c = 137.035\,999\,679$ a.u. and $M = 7294.299$ a.u.

II. CALCULATING THE WAVE FUNCTIONS

The variational Monte Carlo calculation is a method of computing the expectation value of an operator,

$$\langle A\rangle = \sum_i [\Psi(\mathbf{x}_i)A\Psi(\mathbf{x}_i)/w(\mathbf{x}_i)] \Big/ \sum_i [\Psi(\mathbf{x}_i)^2/w(\mathbf{x}_i)], \tag{1}$$

and its standard deviation (i.e., statistical error),

$$\sigma^2 = \sum_i \{[A\Psi(\mathbf{x}_i) - \langle A\rangle\Psi(\mathbf{x}_i)]^2\Psi(\mathbf{x}_i)^2/w(\mathbf{x}_i)^2\}/ \left\{\sum_i [\Psi(\mathbf{x}_i)^2/w(\mathbf{x}_i)]\right\}^2, \tag{2}$$

using Monte Carlo integration. Here $\Psi(\mathbf{x}_i)$ is the value of the trial wave function at the Monte Carlo integration point $\mathbf{x}_i$ and the weight function $w(\mathbf{x}_i)$ is the relative probability of choosing this point. In a variational Monte Carlo calculation the adjustable parameters in the trial wave function are often optimized with respect to a functional, usually some combination of the energy and its standard deviation [66,67].

In Ref. [62] we showed that an exponential pade form produced rapidly convergent energies for the three lowest states of the helium atom with symmetry ^1S, ^1P, ^1D, ^3S, ^3P, and ^3D. The spatial part of these wave functions have the form

$$\Psi_{1S} = (1 \pm P_{12})\exp(\mathcal{P} - \alpha r_1 - \beta r_2), \tag{3}$$

$$\Psi_{2S} = (1 \pm P_{12})(r_1 + a)\exp(\mathcal{P} - \alpha r_1 - \beta r_2), \tag{4}$$

$$\Psi_{3S} = (1 \pm P_{12})\big(r_1^2 + a r_1 + b\big)\exp(\mathcal{P} - \alpha r_1 - \beta r_2), \tag{5}$$

$$\Psi_{2P} = (1 \pm P_{12}) z_1 \exp(\mathcal{P} - \alpha r_1 - \beta r_2), \tag{6}$$

$$\Psi_{3P} = (1 \pm P_{12}) z_1 (r_1 + a)\exp(\mathcal{P} - \alpha r_1 - \beta r_2), \tag{7}$$

$$\Psi_{4P} = (1 \pm P_{12}) z_1 \big(r_1^2 + a r_1 + b\big)\exp(\mathcal{P} - \alpha r_1 - \beta r_2), \tag{8}$$

$$\begin{aligned}\Psi_{3D} = (1 \pm P_{12})\big[&\big(3z_1^2 - r_1^2\big)\exp(\mathcal{P} - \alpha r_1 - \beta r_2)\\ &+ d(2z_1 z_2 - x_1 x_2 - y_1 y_2)\exp(\mathcal{P}_2 - \gamma r_1 - \delta r_2)\big],\end{aligned} \tag{9}$$

$$\begin{aligned}\Psi_{4D} = (1 \pm P_{12})\big[&\big(3z_1^2 - r_1^2\big)(r_1 + a)\exp(\mathcal{P} - \alpha r_1 - \beta r_2)\\ &+ d(2z_1 z_2 - x_1 x_2 - y_1 y_2)(r_1 + b)\exp(\mathcal{P}_2 - \gamma r_1 - \delta r_2)\big],\end{aligned} \tag{10}$$

$$\begin{aligned}\Psi_{5D} = (1 \pm P_{12})\big[&\big(3z_1^2 - r_1^2\big)\big(r_1^2 + a r_1 + b\big)\exp(\mathcal{P} - \alpha r_1\\ &- \beta r_2) + d(2z_1 z_2 - x_1 x_2 - y_1 y_2)\big(r_1^2 + e r_1\\ &+ f\big)\exp(\mathcal{P}_2 - \gamma r_1 - \delta r_2)\big],\end{aligned} \tag{11}$$

where

$$\mathcal{P} = \frac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m}, \quad \mathcal{P}_2 = \frac{\sum_{k=0} c_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} d_k r_1^n r_2^l r_{12}^m}. \tag{12}$$

Here the operator P_{12} interchanges the two electrons. The exponents l, m, and n are integers $(0, 1, \ldots)$ and all possible terms adding up to $N = n + l + m$ are selected. In Eq. (12) both the numerator and the denominator of the $\mathcal{P}$ terms have the same number of terms.

The parameters in each trial wave function form are adjusted so as to minimize the standard deviation in the local energy [Eq. (2) with $A = H$]. This calculation is done over a set of 16 000 Monte Carlo integration points that are generated from a guiding function that was optimized specifically for each state [68]. Once the adjustable parameters were found, we then evaluated the energy using our largest ($N = 4$) wave function and a set of 65 536 000 Monte Carlo integration points in order to make the statistical error as low as possible. The results, shown in Table I, are all within a microhartree (or better) of the benchmark values given by Drake [69].

TABLE I. Energies (in a.u.) of select helium states computed using our largest wave function ($N = 4$) and 65 536 000 Monte Carlo integration points. Value in the parentheses are statistical errors.

State	Nonrelativistic energy	Relativistic energy
$1\,{}^1S$	−2.903 724 372(5)	−2.903 806 4(2)
	−2.903 724 377 034 119 5 [69]	
$2\,{}^1S$	−2.145 973 51(3)	−2.146 080 4(3)
	−2.145 974 046 054 419 [69]	
$3\,{}^1S$	−2.061 271 55(5)	−2.061 378 1(4)
	−2.061 271 989 740 911 [69]	
$2\,{}^1P$	−2.123 842 89(7)	−2.123 947 3(4)
	−2.123 843 086 498 093 [69]	
$3\,{}^1P$	−2.055 146 04(8)	−2.055 251 6(6)
	−2.055 146 362 091 94 [69]	
$4\,{}^1P$	−2.031 069 82(3)	−2.031 386 7(8)
	−2.031 069 650 450 24 [69]	
$3\,{}^1D$	−2.055 620 725(3)	−2.055 726 9(8)
	−2.055 620 732 852 246 [69]	
$4\,{}^1D$	−2.031 279 815(7)	−2.031 386 7(8)
	−2.031 279 846 178 687 [69]	
$5\,{}^1D$	−2.020 015 828(3)	−2.020 121(1)
	−2.020 015 836 159 984 [69]	
$2\,{}^3S$	−2.175 229 376(3)	−2.175 343 4(2)
	−2.175 229 378 236 791 30 [69]	
$3\,{}^3S$	−2.068 688 69(4)	−2.068 796 8(4)
	−2.068 689 067 472 457 19 [69]	
$4\,{}^3S$	−2.036 511 62(2)	−2.036 617 8(7)
	−2.036 512 083 098 236 30 [69]	
$2\,{}^3P$	−2.133 164 07(4)	−2.133 280 3(3)
	−2.133 164 190 779 273 [69]	
$3\,{}^3P$	−2.058 080 72(4)	−2.058 188 8(8)
	−2.058 081 084 274 28 [69]	
$4\,{}^3P$	−2.032 324 18(2)	−2.032 429(1)
	−2.032 324 354 296 62 [69]	
$3\,{}^3D$	−2.055 636 282(4)	−2.055 743 3(7)
	−2.055 636 309 453 261 [69]	
$4\,{}^3D$	−2.031 288 842(3)	−2.031 395 5(8)
	−2.031 288 847 501 795 [69]	
$5\,{}^3D$	−2.020 021 027(3)	−2.020 127(1)
	−2.020 021 027 446 911 [69]	

III. CALCULATING THE SPIN-INDEPENDENT RELATIVISTIC CORRECTIONS

If there are no external electric and magnetic fields, the lowest-order spin-independent relativistic corrections [11] consist of the mass velocity term,

$$H_1 = -\frac{1}{8c^2}\sum_i \nabla_i^4, \tag{13}$$

the orbit-orbit (retardation) term,

$$H_2 = -\frac{1}{2c^2}\sum_{i<j} \nabla_i \bullet \left[\frac{(\mathbf{r_i} - \mathbf{r_j})(\mathbf{r_i} - \mathbf{r}_j)}{r_{ij}^3} + \frac{1}{r_{ij}}\right] \bullet \nabla_j, \tag{14}$$

and the one- and two-body Darwin terms,

$$H_4 = \frac{Z\pi}{2c^2}\sum_i \delta(\mathbf{r}_i) - \frac{\pi}{c^2}\sum_{i<j}\delta(\mathbf{r}_i - \mathbf{r}_j). \tag{15}$$

In addition, the finite mass of the nucleus gives rise to several other corrections [11]. The largest of these is the mass polarization term,

$$H_7 = -\frac{1}{M}\sum_{i<j} \nabla_i \bullet \nabla_j. \tag{16}$$

For a helium atom these terms can be evaluated from the expressions

$$\langle H_1\rangle = -\frac{1}{4c^2}\int \big(\nabla_1^2\Psi\big)^2 d\tau, \tag{17}$$

$$\langle H_2\rangle = -\frac{1}{2c^2}\int\left[\frac{(\nabla_1\Psi \bullet \mathbf{r}_{12})(\nabla_2\Psi \bullet \mathbf{r}_{12})}{r_{12}^3} + \frac{\nabla_1\Psi \bullet \nabla_2\Psi}{r_{12}}\right] d\tau, \tag{18}$$

$$\langle H_4\rangle = \frac{2\pi}{c^2}\int \Psi\delta(\mathbf{r}_1)\Psi d\tau - \frac{\pi}{c^2}\int \Psi\delta(\mathbf{r}_{12})\Psi d\tau, \tag{19}$$

and

$$\langle H_7\rangle = -\frac{1}{M}\int \nabla_1\Psi \bullet \nabla_2\Psi d\tau. \tag{20}$$

TABLE II. Relativistic corrections of select helium states computed using our largest wave functions ($N = 4$) and 65 536 000 Monte Carlo integration points. Values in the parentheses are statistical errors.

State	H_1	H_2	H_{3Z}	H_{3e}	H_4	H_5	H_6	H_7
$1\,^1S$	−0.000 720 0(2)	−0.00000744(2)	0.0	0.0	0.00058799(9)	0.0	0.000035581(6)	+0.000021810(1)
	−0.000 720 057 889 [14]	−0.000 007 406 982 [14]			0.000 587 953 385 [14]		0.000 035 580 189 [14]	+0.000 021 807 367 [14]
	−0.000 708(2) [64]	−0.000 008 07(3) [64]			0.000 575(2) [64]		0.000 036 5(2) [64]	+0.000 021 4(1) [64]
$2\,^1S$	−0.000 547 2(3)	−0.000 000 483(2)	0.0	0.0	0.000 436 6(1)	0.0	0.000 002 889 4(7)	+0.000 001 247(1)
	−0.000 547 405 942 [14]	−0.000 000 491 699 [14]			0.000 436 683 000 [14]		0.000 002 893 664 [14]	+0.000 001 302 917 [14]
	−0.000 547 406 126 [15]	−0.000 000 492 737 [15]			0.000 436 683 066 [15]		0.000 002 893 682 [15]	+0.000 001 302 917 [15]
$3\,^1S$	−0.000 536 5(4)	−0.000 000 135 1(6)	0.0	0.0	0.000 429 0(1)	0.0	0.000 000 816 2(2)	+0.000 000 336 7(3)
	−0.000 536 731 188 [14]	−0.000 000 136 463 [14]			0.000 428 913 000 [14]		0.000 000 814 149 [14]	+0.000 000 360 633 [14]
$2\,^1P$	−0.000 533 5(4)	−0.000 001 083(1)	0.0	0.0	0.000 426 2(2)	0.0	0.000 000 2448(6)	+0.000 006 319(1)
	−0.000 534 071 057 [15]	−0.000 001 082 625 [15]			0.000 426 273 611 [15]		0.000 000 245 978 [15]	+0.000 006 312 399 [15]
$3\,^1$P	−0.000 532 6(6)	−0.000 000 355 7(4)	0.0	0.0	0.000 426 1(2)	0.0	0.000 000 845 41(2)	+0.000 001 984 0(5)
	−0.000 533 119 004 [15]	−0.000 000 356 644 [15]			0.000 426 098 282 [15]		0.000 000 843 212 [15]	+0.000 001 994 441 [15]
$4\,^1P$	−0.000 531 2(8)	−0.000 000 175 6(3)	0.0	0.0	0.000 426 3(3)	0.0	0.000 000 042 0(1)	+0.000 000 848 4(2)
	−0.000 532 796 474 [15]	−0.000 000 155 402 [15]			0.000 426 047 686 [15]		0.000 000 037 294 [15]	+0.000 000 857 509 [15]
$3\,^1D$	−0.000 532 0(7)	+0.000 000 006 3(6)	0.0	0.0	0.000 426 1(2)	0.0	0.000 000 000 737 3(2)	−0.000 000 033 74(8)
	−0.000 532 602 976 [15]	+0.000 000 006 478 [15]			0.000 425 963 697 [15]		0.000 000 000 765 [15]	−0.000 000 034 191 [15]
$4\,^1D$	−0.000 532 9(8)	+0.000 000 002 7(2)	0.0	0.0	0.000 426 1(2)	0.0	0.000 000 000 437 3(1)	−0.000 000 017 14(4)
	−0.000 532 575 405 [15]	+0.000 000 002 953 [15]			0.000 425 989 179 [15]		0.000 000 000 450 [15]	−0.000 000 017 709 [15]
$5\,^1D$	−0.000 532(1)	+0.000 000 001 7(2)	0.0	0.0	0.000 426 6(2)	0.0	0.000 000 000 254 6(1)	−0.000 000 010 01(3)
	−0.000 532 552 698 [15]	+0.000 000 001 564 [15]			0.000 425 999 278 [15]		0.000 000 000 262 [15]	−0.000 000 009 854 [15]
2^3S	−0.000 556 8(2)	−0.000 000 086(1)	0.0	0.0	0.000 441 86(7)	0.0	0.0	+0.000 001 019 9(6)
	−0.000 556 949 846 [14]	−0.000 000 086 544 [14]			0.000 441 775 001 [14]			+0.000 001 019 046 [14]
	−0.000 556 949 634 [15]	−0.000 000 086 716 [15]			0.000 441 775 301 [15]			+0.000 001 020 267 [15]
3^3S	−0.000 538 5(4)	−0.000 000 025 0(4)	0.0	0.0	0.000 430 3(1)	0.0	0.0	+0.000 000 245 7(1)
	−0.000 538 843 090 [15]	−0.000 000 026 756 [14]			0.000 429 966 045 [14]			+0.000 000 259 162 [14]
4^3S	−0.000 534 3(6)	−0.000 000 009 9(2)	0.0	0.0	0.000 428 1(2)	0.0	0.0	+0.000 000 091 46(5)
	−0.000 535 020 232 [15]	−0.000 000 010 926 [14]			0.000 427 554 541 [14]			+0.000 000 101 318 [15]
2^3P	−0.000 527 5(3)	+0.000 001 864(1)	−0.000 001 844(1)	0.000 002 739 8(7)	0.000 421 2(1)	−0.000 001 199 3(6)	0.0	−0.000 008 848(2)
	−0.000 527 832 255 [15]	+0.000 001 868 104 [15]	−0.000 001 845 649 [15]	0.000 002 741 276 [15]	0.000 4211 996 85 [15]	−0.000 001 199 229 [15]		−0.000 008 852 451 [15]
3^3P	−0.000 530 1(8)	+0.000 000 553 8(6)	−0.000 000 536 1(5)	0.000 000 784 3(2)	0.000 424 9(2)	−0.000 000 328 8(2)	0.0	−0.000 002 543 7(6)
	−0.000 531 346 019 [15]	+0.000 000 550 870 [15]	−0.000 000 535 313 [15]	0.000 000 782 670 [15]	0.000 424 632 958 [15]	−0.000 000 327 895 [15]		−0.000 002 518 268 [15]
4^3P	−0.000 530(1)	+0.000 000 230 3(3)	−0.000 000 222 6(3)	0.000 000 323 6(1)	0.000 426 0(3)	−0.000 000 134 2(2)	0.0	−0.000 001 045 5(3)
	−0.000 532 064 998 [15]	+0.000 000 229 478 [15]	−0.000 000 222 481 [15]	0.000 000 323 367 [15]	0.000 425 441 455 [15]	−0.000 000 133 622 [15]		−0.000 001 035 765 [15]
3^3D	−0.000 532 5(6)	+0.000 000 006 5(5)	−0.000 000 066 74(3)	0.000 000 099 85(4)	0.000 425 8(2)	−0.000 000 065 56(7)	0.0	+0.000 000 003 68(8)
	−0.000 532 588 646 [15]	+0.000 000 007 044 [15]	−0.000 000 066 773 [15]	0.000 000 099 985 [15]	0.000 425 953 220 [15]	−0.000 000 065 478 [15]		+0.000 000 003 472 [15]
4^3D	−0.000 532 8(8)	−0.000 000 003 1(2)	−0.000 000 028 25(1)	0.000 000 042 26(2)	0.000 426 1(2)	−0.000 000 027 55(3)	0.0	+0.000 000 003 87(4)
	−0.000 532 567 303 [15]	+0.000 000 003 269 [15]	−0.000 000 028 244 [15]	0.000 000 042 283 [15]	0.000 425 983 238 [15]	−0.000 000 027 524 [15]		+0.000 000 004 036 [15]
5^3D	−0.000 532(1)	+0.000 000 001 9(2)	−0.000 000 014 51(1)	0.000 000 021 70(2)	0.000 426 5(2)	−0.000 000 014 19(2)	0.0	+0.000 000 002 42(3)
	−0.000 532 548 071 [15]	+0.000 000 001 743 [15]	−0.000 000 014 476 [15]	0.000 000 021 670 [15]	0.000 425 995 883 [15]	−0.000 000 014 066 [15]		+0.000 000 002 683 [15]

We computed each of these expectation values with our largest wave function ($N = 4$) and 65 536 000 Monte Carlo integration points. To evaluate the one- and two-electron δ functions in H_4 we used the procedure described in Ref. [59]. Because our initial calculations of the mass polarization term, Eq. (20), were dominated by large fluctuations around the origin (which led to a considerable loss of precision for the D states), we evaluated this quantity using the rotation method described in Ref. [62]. Our final results for all these expectation values are given in Table II. As expected from the relative quality of each wave function, it is not surprising that our values are better than those in Ref. [64] but they show small deviations from the benchmark values in Refs. [14] and [15].

IV. CALCULATING THE SPIN-DEPENDENT RELATIVISTIC CORRECTIONS

In the absence of external electric and magnetic fields, the lowest-order spin-dependent relativistic corrections [11] consist of the spin-orbit term,

$$H_{3Z} = \frac{Z}{2c^2}\sum_i\left[\frac{\mathbf{r}_i \times \mathbf{p}_i}{r_i^3}\right]\bullet\mathbf{s}_i, \tag{21}$$

the spin-other-orbit term,

$$H_{3e} = \frac{1}{2c^2}\sum_{i\neq j}\left[\frac{\mathbf{r}_{ji}\times\mathbf{p}_i}{r_{ij}^3}\right]\bullet(\mathbf{s}_i + 2\mathbf{s}_j), \tag{22}$$

and the spin-spin terms,

$$H_5 = \frac{1}{c^2}\sum_{i<j}\mathbf{s}_i\bullet\left[\frac{r_{ij}^2 - 3(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)}{r_{ij}^5}\right]\bullet\mathbf{s}_j, \tag{23}$$

$$H_6 = -\frac{8\pi}{3c^2}\sum_{i<j}\delta(\mathbf{r}_i-\mathbf{r}_j)\mathbf{s}_i\bullet\mathbf{s}_j. \tag{24}$$

Before we can evaluate these terms we first have to use the Wigner-Eckhart theorem to separate the spin operators from the spatial operators (see, for example, Refs. [70] and [71]). For the helium atom this allows us to rewrite the spin-orbit, the spin-other-orbit, and the spin-spin terms as

$$\begin{aligned}\langle H_{3Z}\rangle &= \langle LSJM|H_{3Z}|LSJM\rangle\\ &= \frac{2}{c^2}(-1)^{L+S+J}\begin{Bmatrix} J & S & L\\ 1 & L & S\end{Bmatrix}\left\langle L\left\|\frac{\mathbf{r}_1\times\mathbf{p}_1}{r_1^3}\right\|L\right\rangle\langle S\|\mathbf{s}_1\|S\rangle\\ &= \frac{\sqrt{6}}{c^2}(-1)^L\frac{\begin{Bmatrix} L & 1 & L\\ 1 & L & 1\end{Bmatrix}}{\begin{pmatrix} L & 1 & L\\ -1 & 0 & 1\end{pmatrix}}\int\Psi^*(L, M_L = 1)\\ &\quad\times\frac{i\left(y_1\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial y_1}\right)}{r_1^3}\Psi(L, M_L = 1)d\tau,\end{aligned} \tag{25}$$

$$\begin{aligned}\langle H_{3e}\rangle &= \langle LSJM|H_{3e}|LSJM\rangle\\ &= \frac{1}{c^2}(-1)^{L+S+J}\begin{Bmatrix} J & S & L\\ 1 & L & S\end{Bmatrix}\left\langle \mathrm{L}\left\|\frac{\mathbf{r}_{21}\times\mathbf{p}_1}{r_{12}^3}\right\|L\right\rangle\\ &\quad\times\langle S\|\mathbf{s}_1 + 2\mathbf{s}_2\|S\rangle\\ &= \frac{3\sqrt{6}}{2c^2}(-1)^L\frac{\begin{Bmatrix} L & 1 & L\\ 1 & L & 1\end{Bmatrix}}{\begin{pmatrix} L & 1 & L\\ -1 & 0 & 1\end{pmatrix}}\int\Psi^*(L, M_L = 1)\\ &\quad\times\frac{i\left(y_{21}\frac{\partial}{\partial x_1} - x_{21}\frac{\partial}{\partial y_1}\right)}{r_{12}^3}\Psi(L, M_L = 1)d\tau,\end{aligned} \tag{26}$$

$$\begin{aligned}\langle H_5\rangle &= \langle LSJM|H_5|LSJM\rangle\\ &= \frac{1}{c^2}(-1)^{L+S+J}\begin{Bmatrix} J & S & L\\ 2 & L & S\end{Bmatrix}\langle L\|T_2\|L\rangle\langle S\|U_2\|S\rangle\\ &= \frac{\sqrt{30}}{4c^2}(-1)^{L+1}\frac{\begin{Bmatrix} L & 1 & L\\ 2 & L & 1\end{Bmatrix}}{\begin{pmatrix} L & 2 & L\\ 0 & 0 & 0\end{pmatrix}}\int\Psi(L, M_L = 0)\\ &\quad\times\frac{\mathbf{r}_{12}^2 - 3z_{12}^2}{r_{12}^5}\Psi(L, M_L = 0)\,d\tau,\end{aligned} \tag{27}$$

and

$$\begin{aligned}\langle H_6\rangle &= \langle LSJM|H_6|LSJM\rangle\\ &= -\frac{8\pi}{3c^2}\langle L|\delta(\mathbf{r}_{12})|L\rangle\langle S|\mathbf{s}_1\bullet\mathbf{s}_2|S\rangle\\ &= \frac{2\pi}{c^2}\int\Psi(L, M_L = 0)\delta(\mathbf{r}_{12})\Psi(L, M_L = 0)\,d\tau.\end{aligned} \tag{28}$$

Here we denote a reduced matrix element with a double vertical bar, a 6-J symbol with a curly bracket, and a 3-J symbol with a smooth bracket. Following the choice made in Ref. [15], all of these spin-dependent expectation values assume that $J = L$. As before, the two-electron δ function in Eq. (28) is evaluated using the procedure described in Ref. [59].

Because of symmetry, the spin part of Eq. (28) is identically zero for triplets. Similarly, the spatial part of Eqs. (25)–(27) is identically zero for S states or when the trial wave function has $M_L = 0$. Since all of our trial wave functions have $M_L = 0$, we first had to modify our P and D forms to have $M_L = 1$ before we could calculate the spin-orbit and spin-other-orbit terms. For the P states this modification simply replaces the term $Y_{10}(\mathbf{r}_1)Y_{00}(\mathbf{r}_2) = z_1$ with $Y_{11}(\mathbf{r}_1)Y_{00}(\mathbf{r}_2) = x_1 + iy_1$. All of the optimized parameters in the exponential are unaltered. Performing a similar operation on our D states is slightly more complicated because the Clebsch-Gordon expansion produces two combinations of spherical harmonics that add up to $L = 2$; this is what necessitates the second expansion in each of these wave functions. The total angular momentum of the first expansion is given by $Y_{20}(\mathbf{r}_1)Y_{00}(\mathbf{r}_2) = 3z_1^2 - r_1^2$, which we can easily replace with $Y_{21}(\mathbf{r}_1)Y_{00}(\mathbf{r}_2) = z_1(x_1 + iy_1)$. In the second expansion the total angular momentum is given by

$$\begin{aligned}r_1r_2&\left[\sqrt{\frac{3}{2}}Y_{10}(\mathbf{r}_1)Y_{10}(\mathbf{r}_2) + \frac{1}{2}\sqrt{\frac{3}{2}}Y_{11}(\mathbf{r}_1)Y_{1-1}(\mathbf{r}_2)\right.\\ &\left.+\frac{1}{2}\sqrt{\frac{3}{2}}Y_{1-1}(\mathbf{r}_1)Y_{11}(\mathbf{r}_2)\right] = d[2z_1z_2 - x_1x_2 - y_1y_2],\end{aligned} \tag{29}$$

and the $M_L = 1$ analog of this is

$$r_1 r_2 \left[\sqrt{\frac{3}{2}} Y_{10}(\mathbf{r}_1) Y_{11}(\mathbf{r}_2) + \sqrt{\frac{3}{2}} Y_{11}(\mathbf{r}_1) Y_{10}(\mathbf{r}_2) \right] = d[z_1(x_2 + iy_2) + (x_1 + iy_1)z_2]. \tag{30}$$

Although the wave functions needed to evaluate Eqs. (25) and (26) are complex, the imaginary component of the expectation value is zero.

After making all of these adjustments to our trial wave functions we computed the spin-dependent relativistic corrections using our largest wave function ($N = 4$) and 65 536 000 Monte Carlo integration points. As shown in Table II, most of our results agree with the benchmark values given in Ref. [15] to three significant digits. We should point out that the value for the $3D$ state given in Table XV of Ref. [15] is almost certainly a misprint because it would otherwise differ from ours by an order of magnitude. The corrected value for the $\langle H_{3e} \rangle$ matrix element, 1.877 615 241 1, has been used to compute the entry in Table II.

V. CALCULATING THE SINGLET-TRIPLET MIXING

In addition to the changes to each energy level due to the corrections described in the previous sections, the spin-orbit operators cause a small mixing to take place between a singlet wave function and its triplet counterpart [6,10,12]. Using first-order perturbation theory the matrix elements associated with this mixing are [15]

$$\begin{aligned}\langle H_{3Z} \rangle_{\mathrm{ST}} &= \langle LS'JM | H_{3Z} | LSJM \rangle \\ &= \frac{2}{c^2}(-1)^{L+S'+J} \begin{Bmatrix} J & S' & L \\ 1 & L & S \end{Bmatrix} \left\langle L \left\| \frac{\mathbf{r}_1 \times \mathbf{p}_1}{r_1^3} \right\| L \right\rangle \langle S' \| \mathbf{s}_1 \| S \rangle \\ &= \frac{\sqrt{3}}{c^2}(-1)^{L} \frac{\begin{Bmatrix} L & 0 & L \\ 1 & L & 1 \end{Bmatrix}}{\begin{pmatrix} L & 1 & L \\ -1 & 0 & 1 \end{pmatrix}} \int \Psi^*_{\mathrm{singlet}}(L, M_L = 1) \\ &\quad \times \frac{i\left(y_1 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial y_1}\right)}{r_1^3} \Psi_{\mathrm{triplet}}(L, M_L = 1) d\tau,\end{aligned} \tag{31}$$

$$\begin{aligned}\langle H_{3e} \rangle_{\mathrm{ST}} &= \langle LS'JM | H_{3e} | LSJM \rangle \\ &= \frac{1}{c^2}(-1)^{L+S'+J} \begin{Bmatrix} J & S' & L \\ 1 & L & S \end{Bmatrix} \left\langle L \left\| \frac{\mathbf{r}_{21} \times \mathbf{p}_1}{r_{12}^3} \right\| L \right\rangle \\ &\quad \times \langle S' \| \mathbf{s}_1 + 2\mathbf{s}_2 \| S \rangle \\ &= \frac{\sqrt{3}}{2c^2}(-1)^{L-1} \frac{\begin{Bmatrix} L & 0 & L \\ 1 & L & 1 \end{Bmatrix}}{\begin{pmatrix} L & 1 & L \\ -1 & 0 & 1 \end{pmatrix}} \int \Psi^*_{\mathrm{singlet}}(L, M_L = 1) \\ &\quad \times \frac{i\left(y_{21} \frac{\partial}{\partial x_1} - x_{21} \frac{\partial}{\partial y_1}\right)}{r_{12}^3} \Psi_{\mathrm{triplet}}(L, M_L = 1) d\tau.\end{aligned} \tag{32}$$

As before, symmetry considerations cause these terms to vanish for all S states.

We computed each of these expectation values using our largest wave function ($N = 4$) and 65 536 000 Monte Carlo integration points. Because the singlet and triplet wave functions have different guiding functions, we performed our calculations with the more diffuse function. Our results are given in Table III and are in good agreement with the benchmark values given in Drake and Yan [15] once the latter have been corrected for a slight mistake. The singlet-triplet mixing listed in Tables XIV and XV of Ref. [15] were computed with the 6-J symbol $\{\begin{smallmatrix} L & 0 & L \\ 1 & L & 0 \end{smallmatrix}\}$ rather than $\{\begin{smallmatrix} L & 0 & L \\ 1 & L & 1 \end{smallmatrix}\}$ [72]. The corrected values have been used to compute the entries in Table III.

TABLE III. Singlet-triplet mixing coefficients of select helium states computed using our largest wave functions ($N = 4$) and 65 536 000 Monte Carlo integration points. Values in the parentheses are statistical errors.

State	$\langle \mathrm{H}_{3Z} \rangle_{\mathrm{ST}}$	$\langle \mathrm{H}_{3e} \rangle_{\mathrm{ST}}$
$1S$	0.0	0.0
$2S$	0.0	0.0
$3S$	0.0	0.0
$2P$	−0.000 001 907(1)	−0.000 000 689(2)
	−0.000 001 904 968 [15]	−0.000 000 688 043 [15]
$3P$	−0.000 000 560 4(5)	−0.000 000 192 6(9)
	−0.000 000 558 929 [15]	−0.000 000 191 301 [15]
$4P$	−0.000 000 234 6(3)	−0.000 000 079 3(5)
	−0.000 000 234 440 [15]	−0.000 000 078 772 [15]
$3D$	−0.000 000 162 70(7)	−0.000 000 079 96(3)
	−0.000 000 162 750 [15]	−0.000 000 079 992 [15]
$4D$	−0.000 000 068 77(3)	−0.000 000 033 60(2)
	−0.000 000 068 739 [15]	−0.000 000 033 594 [15]
$5D$	−0.000 000 035 33(3)	−0.000 000 017 21(1)
	−0.000 000 035 208 [15]	−0.000 000 017 161 [15]

Now that the mixing coefficients have been determined we can estimate the total relativistic energy for each state as

$$\begin{aligned} E_{\mathrm{rel}} = E_{\mathrm{non}} &+ \langle H_1 \rangle + \langle H_2 \rangle + \langle H_{3Z} \rangle + \langle H_{3e} \rangle + \langle H_4 \rangle + \langle H_5 \rangle \\ &+ \langle H_6 \rangle + \langle H_7 \rangle + \langle H_{3Z} \rangle_{\mathrm{ST}} + \langle H_{3e} \rangle_{\mathrm{ST}}. \end{aligned} \tag{33}$$

Each of these expectation values has a statistical error and a systematic error arising from the use of an approximate trial wave function. Except for the ground state, the relativistic energy estimates in Table I are dominated by the systematic error in our nonrelativistic energies.

VI. CONCLUSIONS

The helium atom has long served as a testing ground for both theoretical and experimental studies and several superb reviews have chronicled the progress in both areas (see, for example, Ref. [73]). In this article we have outlined the steps needed to calculate the lowest-order relativistic corrections to the three lowest states of the helium atom with symmetry ^1S, ^1P, ^1D, ^3S, ^3P, and ^3D using Monte Carlo methods. Starting from a novel set of explicitly correlated trial wave functions that produce a nonrelativistic energy with an accuracy of a microhartree or better, we were able to calculate most of these corrections to two or more significant figures. On a Linux box running at 1150 MHz, evaluating all of the expectation values in this article required less than 50 MB of memory and 10 h of CPU time. Although our results are clearly less accurate than those obtained by several earlier calculations (e.g., Ref. [15]), this is due to the quality of our trial wave functions. One advantage of a Monte Carlo calculation, however, is that the techniques described here can easily be applied to larger atoms and molecules and to wave functions that cannot be analytically integrated. Another advantage is that the time required to numerically evaluate an expectation value will scale much more favorably as the system size increases (approximately N^3 where N is the number of electrons) than most traditional methods [58,74]. Earlier results for large singlet S state atoms suggest that Monte Carlo methods can produce first-order relativistic corrections that are as good or better than those found by these other methods [64]. In a future work we will examine these properties for a variety of atoms.

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