

Spectral representation of the three-body Coulomb problem. I. Nonautoionizing doubly excited states of high angular momentum in helium

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(Received 18 December 2009; published 30 April 2010)

We investigate high-lying doubly excited nonautoionizing states of helium with total angular momentum $L = 1, 2, \dots, 9$ with the help of a configuration interaction approach. We provide highly precise nonrelativistic energies of these states and discuss the properties of the wave functions with respect to the particle exchange operator.

DOI: [10.1103/PhysRevA.81.042527](https://doi.org/10.1103/PhysRevA.81.042527)

PACS number(s): 31.15.ac, 02.70.Hm, 32.30.-r

I. INTRODUCTION

Early spectroscopic experiments [1–3] have revealed the existence of a sharp line at a wavelength of 32.039 nm in the emission spectrum of helium. This line was tentatively ascribed by Kruger to a radiative transition between the $2p^2\ ^3P$ and $1s2p\ ^3P$ states. This interpretation was soon confirmed by Wu [4] on the basis of strong theoretical arguments. In addition and in the same article, Wu also made the correct assumption that the $2p^2\ ^3P$ state is not subject to autoionization. In fact, owing to the conservation requirements on parity and angular momenta, this doubly excited state (DES) has no interaction with the adjacent continuum. When relativistic interactions are taken into account, it acquires an autoionization lifetime, but it is still several orders of magnitude longer than the mean radiative lifetime of the allowed electric dipole transitions. Later on, the existence of this $2p^2\ ^3P$ state of unnatural parity was confirmed by a series of experiments [5–8].

In helium, series of DES of unnatural parity exist. These correspond to a given value of the total angular momentum L . All the states of unnatural parity lying between the first and the second ionization thresholds do not autoionize. By contrast, in H^- , the $2p^2\ ^3P$ state is the only one that is not subject to autoionization. Note that as far as we know, this state has not been observed to date, the problem being the lack of an initial state from which it could be reached [9].

The knowledge of accurate values of the energy and radiative lifetimes of nonautoionizing DES in helium is important in various fields such as astrophysics [10,11] and plasma physics [12–16]. Since the conventional variation procedure does apply in a straightforward way to nonautoionizing DES [17], it is not surprising that the large majority of the calculations are based on variational approaches. See the recent article of Saha and Mukherjee [18] for a comprehensive list of the existing variational calculations. In this article, we calculate the energy of nonautoionizing DES of total angular momentum L ranging from 1 to 9. The calculations are performed by means of a

spectral approach of configuration interaction (CI) type which is not variational. Our approach, which is described in detail in [19,20], combines the complex rotation method with an appropriate expansion of the atom wave function in a basis of products of Coulomb-Sturmian functions of the electron radial coordinates with independent dilation parameters for the two electrons and bipolar spherical harmonics of the angular coordinates. The values of the energies and the widths are obtained within a *single* diagonalization of the atomic Hamiltonian.

This method turned out to be very efficient to calculate both the energy and the width of very asymmetrically singly and doubly excited states of natural parity in helium. It is also extremely well adapted to the calculation of high-lying helium nonautoionizing DES of high angular quantum numbers. Although the complex rotation of the atomic Hamiltonian is, in the present case, unnecessary, it is performed in order to check the accuracy of the results. In addition, the convergence of all these results versus the basis size is systematically analyzed.

This article is divided into two main sections. The first is devoted to a brief description of the relevant aspects of our theoretical approach. In Sec. II, we present and discuss benchmark results for the energy of nonautoionizing DES of total angular momentum L ranging from 1 to 9. Two-dimensional graphs of the probability density of some states are also shown. Unless stated otherwise, atomic units (a.u.) are used throughout this document.

II. THEORETICAL APPROACH

A detailed description of our approach has already been given elsewhere [19–22]. We will thus give only a brief review of its most relevant aspects. For a detailed numerical treatment, the interested reader is referred to [20].

A. Hamiltonian

The nonrelativistic Hamiltonian H for the helium atom—under the assumption of an infinitely heavy nucleus—reads

$$H = \frac{\vec{p}_1^2}{2} + \frac{\vec{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (1)$$

where the nuclear charge $Z = 2$ and \vec{p}_i , r_i , and r_{12} are the momentum and the distance of the electron i to the nucleus and the distance between the two electrons, respectively.

B. Spectral representation

The eigenstate wave function of the helium atom with a total angular momentum L of projection M and total energy E_α satisfies the time-independent Schrödinger equation

$$(H - E_\alpha)\Psi_\alpha^{L,M}(\vec{r}_1, \vec{r}_2) = 0. \quad (2)$$

In our configuration interaction approach [19–21], the solutions of Eq. (2) are expanded in Coulomb-Sturmian functions $S_{n_i, l_i}^{(k_i)}(r_i)$ [23,24] with independent dilation parameters for both electrons for the radial coordinates coupled by bipolar spherical harmonics $\Lambda_{l_1, l_2}^{L,M}(\hat{r}_1, \hat{r}_2)$ [25]:

$$\Psi_\alpha^{L,M}(\vec{r}_1, \vec{r}_2) = \sum_{l_1, l_2} \sum_s \sum_{n_1, n_2} \psi_{k_{1s}, k_{2s}, n_1, n_2, \alpha}^{l_1, l_2, L, M} \times \mathcal{A} \frac{S_{n_1, l_1}^{(k_{1s})}(r_1)}{r_1} \frac{S_{n_2, l_2}^{(k_{2s})}(r_2)}{r_2} \Lambda_{l_1, l_2}^{L,M}(\hat{r}_1, \hat{r}_2), \quad (3)$$

where $\psi_{k_{1s}, k_{2s}, n_1, n_2, \alpha}^{l_1, l_2, L, M}$ is the expansion coefficient and \mathcal{A} is an operator for the projection on singlet or triplet states.

Within a CI approach, the interelectronic distance $1/r_{12}$ is not directly accessible. Instead, one has to exploit the multipole expansion of the electron-electron repulsion:

$$\frac{1}{r_{12}} = \sum_{q=0}^{\infty} \sum_{p=-q}^q \frac{4\pi}{2q+1} \frac{r_{<}^q}{r_{>}^{q+1}} Y_{q,p}^*(\hat{r}_1) Y_{q,p}(\hat{r}_2), \quad (4)$$

with $r_{<} = \min(r_1, r_2)$ and $r_{>} = \max(r_1, r_2)$.

The fact that we allow the dilation parameters and the number of the Coulomb-Sturmian functions associated to electrons 1 and 2 to be different leads to the introduction of a set of Coulomb-Sturmian functions $\{S_{n_1, l_1}^{(k_{1s})}(r_1), S_{n_2, l_2}^{(k_{2s})}(r_2)\}$ associated with electrons 1 and 2, which is characterized by the combination $[k_{1s}, N_{1,s}^{\min}, N_{1,s}^{\max}, k_{2s}, N_{2,s}^{\min}, N_{2,s}^{\max}]$ with $l_1 + N_{1,s}^{\min} \leq n_1 \leq l_1 + N_{1,s}^{\max}$ and $l_2 + N_{2,s}^{\min} \leq n_2 \leq l_2 + N_{2,s}^{\max}$. Moreover, more than one and different sets—labeled by the subscript s —may be selected for any angular configuration (l_1, l_2) .

In order to obtain states of unnatural parity, the L - S coupled individual angular momenta of the electrons have to satisfy $(-1)^{L+1} = (-1)^{l_1+l_2}$. To avoid redundancies in expansion (3), the orbital angular momenta are restricted to $l_1 \leq l_2$, and if $l_1 = l_2$ and $k_{1s} = k_{2s}$, to $n_1 \leq n_2$. Be aware that because of the restriction to $l_1 \leq l_2$, each set of Coulomb-Sturmian functions $[k_{1s}, N_{1,s}^{\min}, N_{1,s}^{\max}, k_{2s}, N_{2,s}^{\min}, N_{2,s}^{\max}]$ should be accompanied by $[k_{2s}, N_{2,s}^{\min}, N_{2,s}^{\max}, k_{1s}, N_{1,s}^{\min}, N_{1,s}^{\max}]$ in the case of $k_{1s} \neq k_{2s}$ and $l_1 \neq l_2$. The reason for this is that, for example, sets with $k_{1s} > k_{2s}$ would explicitly favor a smaller extent of the l_1 orbital than for the l_2 orbital. The inclusion of this additional set leads to a significant reduction of the basis size when angular configurations (l_1, l_2) with $l_1 \neq l_2$ are used.

By choosing appropriate sets of Coulomb-Sturmian functions, the description of a given energy regime, that is, below a certain ionization threshold, is possible with a rather small number of basis functions [20].

C. Complex rotation

Complex rotation (or dilation) [26–31] is widely used to extract the energy and decay rates of resonance states. However, as explained in Sec. III, it can also be used as an additional convergence test (together with the variation of the basis size and of the dilation parameters k_{1s}, k_{2s}).

Effectively complex rotation is given by a rotation of the position and momentum operators in the complex plane according to

$$\begin{aligned} \vec{r} &\rightarrow \vec{r} \exp(i\theta), \\ \vec{p} &\rightarrow \vec{p} \exp(-i\theta), \end{aligned} \quad (5)$$

which leads to a non-Hermitian Hamiltonian with complex eigenvalues. The spectrum of the rotated Hamiltonian has the following important properties [27,29,31]:

(i) The bound spectrum of H is invariant under the complex rotation.

(ii) The continuum states are located on half-lines, rotated by an angle -2θ around the ionization thresholds of the unrotated Hamiltonian into the lower half of the complex plane. In the specific case of the unperturbed helium Hamiltonian (1), the continuum states are rotated around the single ionization threshold $I_N = -2/N^2$ [32], with $N \in \mathbb{N}$.

(iii) There are isolated complex eigenvalues $E_{i,\theta} = E_i - i\Gamma_i/2$ in the lower half-plane, corresponding to resonance states. These are stationary under changes of θ , provided the dilation angle is large enough to uncover their positions on the Riemannian sheets of the associated resolvent [32,33]. The associated resonance eigenfunctions are square integrable [30], in contrast to the resonance eigenfunctions of the unrotated Hamiltonian. The latter are asymptotically diverging, outgoing waves [30,34,35].

III. RESULTS

For total angular momentum L , individual angular momenta of the electrons satisfy the relation $(-1)^{L+1} = (-1)^{l_1+l_2}$ for unnatural parity states. As a consequence of this and of the triangular condition for the addition of angular momenta, the single-particle angular momentum cannot be zero ($l_i \neq 0, i = 1, 2$), the total angular momentum is at least 1, and the lower electron excitation must be at least $n_i = 2$. Therefore the series of bound states of unnatural parity states converges to the second ionization threshold. Energies of singlet and triplet nonautoionizing helium DES of unnatural parity, $2pnl$, for $L = 1, \dots, 9$ are presented in Tables I and II. These have been obtained after diagonalization of the matrix representation of (2) in the basis described in Sec. II. We have used up to 26 angular configurations (l_1, l_2) , which lead to matrix dimensions up to 16000×16000 (most of the results presented here converge with a $10\times$ smaller basis). The presented data have been tested for convergence with respect to variation of the complex rotation angle θ , the dilation parameters, and the number of angular configurations. In particular, these energies

TABLE I. Absolute values of the energies [$-E$ (a.u.)] of nonautoionizing doubly excited $1P^e, 3P^e, 1D^o, 3D^o, 1F^e$, and $3F^e$ states of helium in comparison with reference data.

n	$1P^e$			$3P^e$			$1D^o$			$3D^o$		
	Present work	Ref. data	Present work	Ref. data	n	Present work	Ref. data	Present work	Ref. data	Present work	Ref. data	
2	0.580 246 471 5	0.580 246 472 594 ^a	0.710 499 8	0.710 500 155 678 3 ^a	3	0.563 800 418	0.563 800 420 462 ^a	0.559 328 24	0.559 328 263 096 ^a	0.559 328 24	0.559 328 263 096 ^a	
3	0.580 246 471 5	0.580 246 472 594 38 ^b	0.567 812 81	0.567 812 898 724 ^a	4	0.534 576 384 8	0.534 576 385 556 ^a	0.532 678 59	0.532 678 601 895 ^a	0.532 678 59	0.532 678 601 895 ^a	
4	0.540 041 590 5	0.540 041 590 09 ^a	0.535 867 15	0.535 867 188 7 ^a	5	0.521 659 015 1	0.521 659 015 466 ^a	0.520 703 455	0.520 703 462 028 ^a	0.520 703 455	0.520 703 462 028 ^a	
5	0.524 178 981 6	0.524 179 0 ^a	0.522 254 56	0.522 254 57 ^a	6	0.514 833 593 0	0.514 833 593 21 ^a	0.514 288 303	0.514 288 306 62 ^a	0.514 288 303	0.514 288 306 62 ^a	
6	0.516 208 610 3	0.524 178 981 811 41 ^b	0.515 160 194	0.522 254 575 707 23 ^b	7	0.510 792 619 0	0.510 792 619 1 ^a	0.510 452 854	0.510 452 856 7 ^a	0.510 792 619 0	0.510 452 856 7 ^a	
7	0.511 626 536 29	0.516 208 610 468 18 ^b	0.510 991 685	0.515 160 203 854 35 ^b	8	0.508 203 763 91	0.510 787 23 ^d	0.507 977 983 1	0.507 978 0 ^a	0.508 203 763 91	0.507 978 0 ^a	
8	0.508 748 011 46	0.511 626 536 377 82 ^b	0.508 334 233	0.510 991 691 207 13 ^b	9	0.506 446 071 46	0.508 015 48 ^d	0.506 288 496 5	0.507 945 30 ^d	0.508 334 233	0.507 945 30 ^d	
9	0.506 821 044 38	0.508 748 011 515 96 ^b	0.506 536 276	0.508 334 237 504 62 ^b	10	0.505 198 308 78	0.506 445 ^a	0.505 084 014 0	0.506 287 ^a	0.506 821 044 38	0.506 287 ^a	
10	0.505 467 675 14	0.506 821 044 415 78 ^b	0.505 263 296	0.506 536 279 095 44 ^b	11	0.504 280 701 70		0.504 195 182 2		0.505 467 675 14	0.504 195 182 2	
11	0.504 480 743 92	0.505 467 675 167 22 ^b	0.504 329 079 7	0.505 263 297 737 72 ^b	12	0.503 586 256 06		0.503 520 608 1		0.504 480 743 92	0.503 520 608 1	
12	0.503 738 897 04	0.504 480 743 935 11 ^b	0.503 623 245 4	0.505 263 296	13	0.503 048 058 49		0.502 996 572 4		0.503 738 897 04	0.502 996 572 4	
13	0.503 167 185 27	0.516 208 610 468 18 ^b	0.503 076 976 2	0.515 160 194	14	0.502 622 519 28		0.502 581 397 3		0.503 167 185 27	0.502 581 397 3	
14	0.502 717 278 06	0.511 626 536 377 82 ^b	0.502 645 555 9	0.510 991 685	15	0.502 280 254 61		0.502 246 891 3		0.502 717 278 06	0.502 246 891 3	
15	0.502 356 869 59	0.508 748 011 515 96 ^b	0.502 298 904 4	0.508 334 233	16	0.502 000 872 000		0.501 973 432 00		0.502 356 869 59	0.502 000 872 000	
16	0.502 063 698 74	0.506 821 044 415 78 ^b	0.502 016 182 73	0.506 536 276	17	0.501 769 859 819		0.501 747 019 84		0.502 063 698 74	0.501 769 859 819	
17	0.501 822 020 527	0.505 467 675 167 22 ^b	0.501 782 583 97	0.505 263 296	18	0.501 576 663		0.501 557 450		0.501 822 020 527	0.501 576 663	
18	0.501 620 444	0.504 480 743 935 11 ^b	0.501 587 352	0.504 329 079 7	19	0.501 413		0.501 397 1		0.501 620 444	0.501 413	
19	0.501 450 6	0.504 480 743 935 11 ^b	0.501 422 4	0.504 329 079 7						0.501 450 6	0.501 422 4	

n	$1F^e$			$3F^e$			$1F^e$ (continued)			$3F^e$ (continued)		
	Present work	Ref. data	Present work	Ref. data	n	Present work	Ref. data	Present work	Ref. data	Present work	Ref. data	
4	0.531 995 436 71	0.531 995 436 950 9 ^a	0.531 991 325 1	0.531 991 326 346 5 ^a	12	0.503 500 444 342	0.503 500 444 342	0.503 500 200 79	0.503 500 200 79	0.503 500 444 342	0.503 500 200 79	
5	0.520 385 670 86	0.520 385 671 048 6 ^a	0.520 382 858 3	0.520 382 859 283 9 ^a	13	0.502 980 780 358	0.502 980 780 358	0.502 980 588 47	0.502 980 588 47	0.502 980 780 358	0.502 980 588 47	
6	0.514 113 218 05	0.514 113 218 178 1 ^a	0.514 111 428 4	0.514 111 429 118 0 ^a	14	0.502 568 796 718	0.502 568 796 718	0.502 568 642 90	0.502 568 642 90	0.514 113 218 05	0.502 568 642 90	
7	0.510 345 737 95	0.510 345 738 040 ^a	0.510 344 564 22	0.510 344 564 686 ^a	15	0.502 236 675 558 0	0.502 236 675 558 0	0.502 236 550 40	0.502 236 550 40	0.510 345 737 95	0.502 236 550 40	
8	0.507 907 548 30	0.507 907 548 2 ^a	0.507 906 745 95	0.507 906 746 1 ^a	16	0.501 965 034 303 4	0.501 965 034 303 4	0.501 964 931 12	0.501 964 931 12	0.507 907 548 30	0.501 964 931 12	
9	0.506 239 658 11	0.506 239 653 ^a	0.506 239 088 34	0.506 239 088 34	17	0.501 740 032 588	0.501 740 032 588	0.501 739 946 53	0.501 739 946 53	0.506 239 658 11	0.501 739 946 53	
10	0.505 048 739 15		0.505 048 321 08		18	0.501 551 573 9	0.501 551 573 9	0.501 551 501 4	0.501 551 501 4	0.505 048 739 15	0.501 551 501 4	
11	0.504 168 863 147		0.504 168 547 77		19	0.501 392	0.501 392	0.501 392 1	0.501 392 1	0.504 168 863 147	0.501 392 1	

^aReference [38].^bReference [37].^cReference [39].^dReference [36].

TABLE II. Absolute values of the energies $[-E$ (a.u.)] of nonautoionizing helium states of unnatural parity and total angular momentum $L = 4, \dots, 9$.

n	$^1G^o$	$^3G^o$	$^1H^e$	$^3H^e$	$^1I^o$	$^3I^o$
5	0.520 159 333 525	0.520 159 320 19				
6	0.513 982 240 486	0.513 982 226 81	0.513 936 277 123	0.513 936 277 088	0.510 221 504 5173	0.510 221 504 52
7	0.510 263 292 891	0.510 263 281 69	0.510 234 206 348 6	0.510 234 206 302 1	0.507 824 251 1171	0.507 824 251 117
8	0.507 852 347 306	0.507 852 338 60	0.507 832 802 655 6	0.507 832 802 610 5	0.506 181 130 564 2	0.506 181 130 564 07
9	0.506 200 910 578	0.506 200 903 864	0.506 187 156 601 8	0.506 187 156 562 3	0.505 006 063 822 6	0.505 006 063 822 5
10	0.505 020 507 250	0.505 020 502 034	0.505 010 467 073 0	0.505 010 467 039 7	0.504 140 111 927 5	0.504 140 111 927 5
11	0.504 147 662 468 3	0.504 147 658 368	0.504 140 111 955 27	0.504 140 111 927 5	0.503 478 301 806 55	0.503 478 301 806 55
12	0.503 484 121 657 1	0.503 484 118 391 6	0.503 478 301 829 59	0.503 478 301 806 55	0.502 963 367 453 55	0.502 963 367 453 55
13	0.502 967 947 260 7	0.502 967 944 626	0.502 963 367 472 73	0.502 963 367 453 55	0.502 554 857 271 02	0.502 554 857 271 02
14	0.502 558 525 531 3	0.502 558 523 379 6	0.502 554 857 287 07	0.502 554 857 271 02	0.502 225 344 119 14	0.502 225 344 119 14
15	0.502 228 327 427 2	0.502 228 325 650 0	0.502 225 344 132 65	0.502 225 344 119 14	0.501 955 698 961 6	0.501 955 698 961 6
16	0.501 958 157 688 8	0.501 958 156 205 6	0.501 955 698 971 6	0.501 955 698 961 6	0.501 732 250 837 9	0.501 732 250 837 9
17	0.501 734 301 049 9	0.501 734 299 800	0.501 732 250 837 9	0.501 732 250 837 9	0.501 545 019 34	0.501 545 019 34
18	0.501 546 746 7	0.501 546 745 7	0.501 545 019 35	0.501 545 019 34	0.501 386 58	0.501 386 58
19	0.501 388 05	0.501 388 0	0.501 386 58	0.501 386 58	0.501 251	0.501 251
20	0.501 25	0.501 252	0.501 251	0.501 251		
n	$^1K^e$	$^3H^e$	$^1L^o$	$^3L^o$	$^1M^e$	$^3M^e$
8	0.507 819 924 882 19	0.507 819 924 882 2				
9	0.506 178 079 688 61	0.506 178 079 688 61	0.506 176 367 564 78	0.506 176 367 564 78	0.505 001 822 851 975	0.505 001 822 851 975
10	0.505 003 833 315 58	0.505 003 833 315 58	0.505 002 581 178 723	0.505 002 581 178 723	0.504 133 604 634 452	0.504 133 604 634 452
11	0.504 135 118 758 10	0.504 135 118 758 10	0.504 134 175 798 51	0.504 134 175 798 51	0.503 473 282 119 32	0.503 473 282 119 32
12	0.503 474 450 498 81	0.503 474 450 498 81	0.503 473 722 891 18	0.503 473 722 891 18	0.502 959 414 840 2	0.502 959 414 840 2
13	0.502 960 335 093 75	0.502 960 335 093 75	0.502 959 762 025 69	0.502 959 762 025 69	0.502 551 689 760 7	0.502 551 689 760 7
14	0.502 552 427 384 38	0.502 552 427 384 38	0.502 551 968 057 60	0.502 551 968 057 60	0.502 222 766 979 6	0.502 222 766 979 6
15	0.502 223 367 228 905	0.502 223 367 228 91	0.502 222 993 455 07	0.502 222 993 455 07	0.501 953 574 236 04	0.501 953 574 236 04
16	0.501 954 069 184 93	0.501 954 069 184 93	0.501 953 760 987 1	0.501 953 760 987 07	0.501 730 478 592 4	0.501 730 478 592 4
17	0.501 730 891 481 47	0.501 730 891 481 47	0.501 730 634 385 2	0.501 730 634 385 2	0.501 543 525 784 3	0.501 543 525 784 3
18	0.501 543 873 784 5	0.501 543 873 784 5	0.501 543 657 095 9	0.501 543 657 096	0.501 385 310 287 5	0.501 385 310 287 5
19	0.501 385 606 3	0.501 385 606 3	0.501 385 421 98	0.501 385 421 98	0.501 250 230 502 3	0.501 250 230 502 3
20	0.501 250 5	0.501 250 5	0.501 250 33	0.501 250 33		
21					0.501 133 986 035	0.501 133 986 035

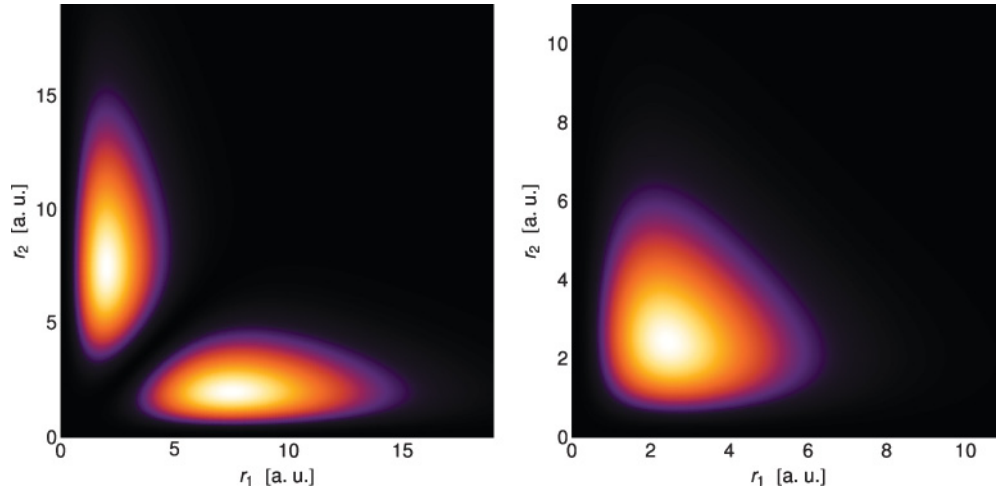


FIG. 1. (Color online) Probability density after integration over the angles of (left) the lowest lying $^1P^e$ state and (right) the lowest lying $^3P^e$ state. In contrast to the states of natural parity, singlet states exhibit a vanishing radial density along $r_1 = r_2$, while the maximum of the density of triplet states has a maximum along this line. This apparent contradiction is an artifact of the angular integration.

are invariant with respect to θ in an exact representation. The variations of the eigenvalues with respect to θ induced by the truncation of the basis are used to find the converged digits. In our calculations, we have used the values of the rotation angle $\theta \in \{0.0, 0.005, 0.01, 0.025, 0.05\}$. Only converged digits are shown in Tables I and II. Note that all values presented in each one of these tables have been obtained with one optimized basis choice.

Low-lying P , D , and F unnatural parity states have been calculated within different approaches [36–40]. In Table I, we reproduce the energies of these states and present more benchmark results for further excited states. Table II displays energies of states with total angular momentum $L = 4, \dots, 9$.¹ As in the case of natural parity states [41], exchange effects can be neglected for sufficiently large values of L . For instance, the singlet-triplet splitting for $n = 10$ goes exponentially fast to zero as $\exp(-4.9L)$.

For symmetric excitation of both electrons, our approach suffers from the influence of the Kato cusp [42], which is a discontinuity of the derivative of the wave function at $r_{12} = 0$ that is not resolvable within our approach. The effect can easily be spotted in our tables as the precision of our results increases with increasing excitation of the outer electron.

Figure 1 shows the radial density integrated over the angles of the lowest lying $^1P^e$ and $^3P^e$ states, respectively. The density plot for the triplet state shows the same behavior as the helium ground state; that is, the density plot exhibits a maximum along the axis $r_1 = r_2$. However, this behavior would be expected for singlet states. This apparent contradiction is a consequence of the integration on the angular coordinates that introduces a sign change. This can be easily understood from the properties of the projector \mathcal{A} of Eq. (3) and of the Clebsch-Gordon coefficients. The projector \mathcal{A} of Eq. (3) is written as $\mathcal{A} = (1 + \epsilon P)/\sqrt{2}$, with P being the operator

that exchanges $[n_1, l_1, k_{1s}] \rightleftharpoons [n_2, l_2, k_{2s}]$ and $\epsilon = \pm 1$. From the relation $\langle l_2 m_2 l_1 m_1 | L M \rangle = (-1)^{l_1 + l_2 - L} \langle l_1 m_1 l_2 m_2 | L M \rangle$, it follows that the wave function (3) is symmetric (antisymmetric) for $\epsilon(-1)^{l_1 + l_2 - L} = 1$ [$\epsilon(-1)^{l_1 + l_2 - L} = -1$]. On the one hand, singlet (triplet) unnatural parity states are characterized by $\epsilon = -1$ ($\epsilon = +1$), that is, exactly the opposite situation as for natural parity states. On the other hand, integration over the angle coordinates of $\Psi_\alpha^{L,M}$ eliminates the sign $(-1)^{l_1 + l_2 - L}$. Thus the structure of the density plots depends exclusively on ϵ , which finally explains the apparent contradiction in Fig. 1.

IV. SUMMARY

A CI expansion of the two-electron wave function in terms of Sturmian functions with independent nonlinear parameters has been used to calculate the energies of nonautoionizing doubly excited helium states for total angular momentum $L = 1, 2, \dots, 9$. Autoionizing P states of unnatural parity are treated elsewhere [43]. Our results are in perfect agreement with existing data for low-lying P , D , and F states. We have also provided insight into the structure of the probability density of such states, and we have discussed an apparent exchange of the symmetry properties with respect to the particle exchange operator as compared with natural parity states.

ACKNOWLEDGMENTS

The work was supported by the Deutsche Forschungsgemeinschaft, Contract No. FR 591/16-1. Access to the computing facilities of the Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaft is gratefully acknowledged. The authors thank the Université catholique de Louvain for providing them with access to the supercomputer of the Calcul Intensif et Stockage de Masse (CISM), which is supported by the FNRS through Fonds de la Recherche Fondamentale et Collective (FRFC) Project No. 2.4556.99, “Simulations Numériques et traitement des données.” J.M. thanks the FNRS for financial support during his stay at the Université catholique de Louvain.

¹Notice that Mihelič [40] has also calculated singlet unnatural parity states up to $n = 15$ and up to $L = 10$, which are in good agreement with our results (not included in our tables).

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