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Mass-polarization effect and oscillator strengths for S,P,D states of helium

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It is well known that including the coordinate r_{12} in the wave function is essential in obtaining highly accurate results for the low-lying bound states of two-electron systems. In this work we calculate the energy, wave function, oscillator strength, radial expectation values, and mass-polarization effect for helium bound states by using simple configuration-interaction basis functions. Our results show that the advantage of the r_{12} coordinate is lost quickly in going from S to D states. In most cases, the results of this work give substantial improvement over previous calculations where r_{12} is not included. For $^{1,3}D$ states the results presented here are among the best in the literature.

INTRODUCTION

The energy and oscillator strengths of the helium bound states have been studied extensively in the literature. Most of the highly accurate results are obtained by the use of perimetric coordinates,[1] or Hylleraas coordinates,[2] where r_{12} is explicitly employed in the basis functions. This enables the wave function to satisfy the cusp condition.[3] The r_{ij} coordinates for three- and four-electron systems have been used in a more restrictive manner for the calculation of some lower-bound states of lithium and beryllium.[4] However, for multielectron problems, including r_{12} explicitly in the basis functions becomes impractical. For these problems the configuration-interaction basis functions are used instead. It is therefore important to find out the limitations of the simpler basis functions by applying them to a two-electron system where accurate results are available for comparison. This has also been done in the literature, notably by Green *et al.*[5] and more recently by Froese Fisher.[6] However, the results thus obtained are significantly inferior to those of Ref. 1, not only in energy, but in oscillator strengths, radial expectation values, etc.

In this work, we use simple configuration-interaction basis functions with a very limited number of nonlinear parameters to calculate the energy, wave function, oscillator strength, radial expectation integrals, and mass-polarization effect of the $1s\,1s\,^1S$, $1s\,2s\,^{3,1}S$, $1s\,2p\,^{3,1}P$, and $1s\,3d\,^{3,1}D$ states of helium. The linear parameters are limited to be from 60 to 110. The results we obtain are substantially better than earlier work with similar types of basis functions in most cases. In the case of the $1s\,3d\,^{3,1}D$ states, the present results are among the best in the literature.

The method of computation, results, and discussion will be given in the following sections. Section I presents the wave function and calculational procedure used. Section II gives the nonrelativistic energy eigenvalues and some expectation values of various radial operators. Section III gives the results for the mass-polarization effect, and Sec. IV presents the oscillator strengths. Finally, Sec. V is a brief summary. In this work we shall only compare our results with a few representative works from the literature. A more complete compilation of references can be found in Godefroid and Verhaegen.[7]

I. WAVE FUNCTION

The radial and angular basis functions used take the form

$$\phi(m,n,\alpha_i,\beta_i\,|\,r_1,r_2) = r_1^m e^{-\alpha_i r_1} r_2^n e^{-\beta_i r_2}\,, \tag{1}$$

$$Y_{l_1l_2}^{LM} = \sum_{m_1m_2} \langle l_1 l_2 m_1 m_2 \,|\, LM\rangle \times Y_{l_1m_1}(\hat{r}_1)Y_{l_2m_2}(\hat{r}_2)\,. \tag{2}$$

The subscript i on the nonlinear parameters α and β in the radial part expresses the fact that different nonlinear parameters are used for each angular partial wave, the angular part being the eigenfunction of total angular momentum L and z component M formed from coupling the two angular momenta, l_1 and l_2, with the Clebsch-Gordan coefficients. The trial wave function is then written:

$$\Psi=A\sum_{m,n;l_1,l_2} C_{mnl_1l_2}\phi(m,n,\alpha_i,\beta_i\,|\,r_1r_2) \times Y^{LM}_{l_1l_2}\chi(1,2)\,, \tag{3}$$

where A is the antisymmetrization operator and $\chi(1,2)$ is the spin function of either singlet or triplet.

Equation (3) is used in performing a Raleigh-Ritz variational calculation, with the nonrelativistic Hamiltonian

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_{12}}\,. \tag{4}$$

The angular correlation is accounted for by the inclusion of an appropriate number of angular partial waves in the trial function. Usually a large number of linear parameters is needed to obtain good convergence for the energy. To keep the number of terms in the wave function down, an efficient radial term selection process has been included in the computer code. It works as follows. First, a large radial basis is chosen for a given angular partial wave, then the energy and wave function are calculated. The terms in this wave function are then ordered according to the magnitudes of the coefficients of the normalized basis functions. The computer code then accesses each term's contribution to the energy in order to decide whether that term should be kept or omitted from the final wave function. Hence, a smaller wave function is obtained which will generate essentially the same energy as the larger one. With this wave function, the energy and expectation values are tabulated.

II. ENERGY EIGENVALUES AND RADIAL INTEGRALS

In Table I we show the convergence of the energy by tabulating the energy contribution obtained from each angular partial wave along with the number of linear parameters employed. For each partial wave a different optimized pair of nonlinear parameters was used. In Table II, the present energies are compared with the most accurate energies available from various calculational methods. In column 1 the highly accurate energies of Pekeris and co-workers[1] are given. The wave functions were expanded with 560 – 1078 terms, where the basis functions employed perimetric coordinates. In column 2 are the results of Weiss[2] who used Hylleraas-type basis functions, with expansions of 52 – 54 terms. Column 3 gives the results of Green's[5] configuration-interaction (CI) expansion in terms of Slater orbitals, where he used expansions of 42 – 50 terms. Froese Fisher's[6] multiconfiguration Hartree-Fock (MCHF) results are given in column 4. In column 5 are Divine and Stewart's[8] results. These were obtained by a perturbation-theory expansion through fourth order in the energy and through second order in the wave functions, where the zero-order wave functions were generated by the frozen core Hartree-Fock approximation. Finally, the present results are given in the last column.

For the ground state the need of the coordinate r_{12} to account for the electron correlation is clearly seen. The present result of $-2.903\,535$ a.u., however, is a significant improvement in the ground-state energy over Refs. 5, 6, and 8. The 2^1S result shows continued need for r_{12} in this low-lying ^1S state. For this state the Green *et al.*[5] result is slightly better than the present calculation in energy but their oscillator strength is poorer (see Table V). For the 2^3S, 2^1P, and 2^3P states our results agree much better with those of Ref. 1, especially for the triplet states. The present calculations for these states are lower than other calculations in which r_{12} is not explicitly used. Finally, for the 3^1D and 3^3D states the energies of the present work are the same to all digits quoted by Weiss who used Hylleraas coordinates. Blanchard and Drake[9] have also calculated these D states with 50-term Hylleraas wave functions. They obtained $-2.055\,620\,1$ and $-2.055\,636\,0$ a.u. for the ^1D and ^3D energies, respectively. The oscillator strengths are not calculated in this reference. The present work shows a slight improvement over these results in the last digit as compared with the experimental results of $-2.055\,620\,9$ and $-2.055\,636\,4$ a.u. as quoted in Ref. 9.

In Table III a comparison of the expectation values of $\frac{1}{2}(1/r_1+1/r_2)$, $\frac{1}{2}(r_1+r_2)$, and $\frac{1}{2}(r_1^2+r_2^2)$ is given. These values give some indication of the accuracy of the wave functions at small, intermediate, and large values of the radial

TABLE I. Convergence of energy eigenvalues [$-E$ in a.u., (l_1,l_2)= angular momenta of electrons in particular partial wave, N= number of term].

(l_1,l_2)	N	$1s1s\,^1S$	N	$1s2s\,^1S$	N	$1s2s\,^3S$	(l_1,l_2)	N	$1s2p\,^1P$	N	$1s2p\,^3P$	(l_1,l_2)	N	$1s3d\,^1D$	N	$1s3d\,^3D$
(0,0)	27	2.878 994 2	42	2.144 184 7	24	2.174 264 3	(0,1)	45	2.122 593 5	50	2.132 368 8	(0,2)	17	2.055 546 54	24	2.055 573 78
(1,1)	32	0.021 484 5	36	0.001 566 0	16	0.000 906 3	(1,2)	30	0.001 092 3	23	0.000 742 0					
(2,2)	18	0.002 229 3	20	0.000 144 8	14	0.000 048 3	(2,3)	20	0.000 105 4	13	0.000 040 0	(1,3)	20	0.000 036 76	18	0.000 035 24
(3,3)	15	0.000 540 4	9	0.000 030 8	9	0.000 006 5	(3,4)	9	0.000 024 4	7	0.000 005 4	(1,1)	9	0.000 034 29	8	0.000 025 25
(4,4)	10	0.000 181 4	2	0.000 006 4	6	0.000 001 3	(4,5)	5	0.000 008 3	4	0.000 001 0	(2,4)	6	0.000 001 33	4	0.000 000 94
(5,5)	4	0.000 067 7	1	0.000 002 6	5	0.000 000 3	(5,6)	1	0.000 002 5			(2,2)	3	0.000 000 99	3	0.000 000 53
(6,6)	2	0.000 025 8			4	0.000 000 1						(3,5)	3	0.000 000 19	5	0.000 000 48
(7,7)	2	0.000 011 4										(3,3)	2	0.000 000 14		
Total	110	2.903 535	110	2.145 935	78	2.175 227		110	2.123 823	97	2.133 157		60	2.055 620 2	62	2.055 636 2

coordinates, respectively. $\langle r^2 \rangle$ also relates to the scattering cross section and diamagnetic susceptibility of the atomic system. The results obtained in this work compare extremely well with those of Pekeris and co-workers,[1] and give order of magnitude improvement over those of Froese Fisher,[6] and Divine and Stewart.[8]

III. MASS POLARIZATION

In the usual nonrelativistic Hamiltonian, Eq. (4), the coordinates $\vec{r}_1$ and $\vec{r}_2$ are relative coordinates, i.e., the position vectors of the electrons relative to the nucleus. In the derivation of the nonrelativistic Hamiltonian[10] the motion of the nucleus manifests itself in two ways. One effect is to change the atomic unit of energy $me^4/\hbar^2=27.211\,652$ eV, where m is the mass of the electron, to $\mu e^4/\hbar^2 = 27.207\,952$ eV, where μ is the reduced mass of the electron in helium. This effect is the same for all levels, raising their energy by the factor $\mu/m = 0.999\,864\,03$. The other effect is an extra term in the nonrelativistic Hamiltonian, $\vec{P}_1\cdot\vec{P}_2/m_n$ (m_n is the nuclear mass in atomic units), that has been neglected in Eq. (4). This mass-polarization effect depends on how the two electron's momenta are correlated, and therefore is different for different levels. For excited two-electron bound states it will be largest for $^1P^o$ states.[10]

The shift in energy due to the mass-polarization effect can be obtained by evaluating the expectation value of $-(1/m_n)\vec{\nabla}_1\cdot\vec{\nabla}_2$. The results of this calculation are given in Table IV along with other results from the literature except for the D states for which no previous results are available. The present results are in good agreement with Pekeris and the other accurate calculations.[11,12]

IV. OSCILLATOR STRENGTHS

The oscillator strength of helium is defined in the dipole-length formula as

$$f_l = 2(E_f - E_i) \times |\langle \psi_f(L',M') | \vec{r}_1 + \vec{r}_2 | \psi_i(L,M) \rangle |^2 , \tag{5}$$

or in the dipole-velocity formula as

$$f_v = 2\frac{1}{(E_f - E_i)} \times |\langle \psi_f(L',M') | \nabla_1 + \nabla_2 | \psi_i(L,M) \rangle |^2 . \tag{6}$$

In the case, where ψ_f and ψ_i have many magnetic

TABLE II. Nonrelativistic energy eigenvalues of helium ($-E$ in a.u.).

State	Perimetric (Ref. 1)	Hylleraas (Ref. 2)	CI (Ref. 5)	MCHF (Ref. 6)	Perturbation (Ref. 8)	Present
1^1S	2.903 724	2.903 72	2.903 383	2.903 033	2.903 433	2.903 535
2^1S	2.145 974	2.145 97	2.145 938	2.145 873	2.145 909	2.145 935
2^3S	2.175 229	2.175 23	2.175 214	2.175 218	2.175 225	2.175 227
2^1P	2.123 843	2.123 84	2.123 782	2.123 748[a]	2.123 801	2.123 826
2^3P	2.133 164	2.133 16	2.133 128	2.133 086	2.133 153	2.133 157
3^1D		2.055 62	2.055 615	2.055 618	2.055 617	2.055 620
3^3D		2.055 64	2.055 630	2.055 635	2.055 633	2.055 636

[a] Quoted in M. Godefroid and G. Verhaegan (see Ref. 7).

substates, the experimental result usually corresponds to the average of all possible transitions, that is, a sum over the final states and an average over the initial states. This result can be obtained by applying the Wigner-Eckart theorem to the matrix element of a single transition. For example, for the case where the initial and final angular momenta L and L' are different we can use the transition matrix element of z that connects the $M=M'=0$ magnetic substates, Eqs. (5) and (6) become

TABLE III. Radial expectation values for bound states of helium (in a.u.).

State		Perimetric (Ref. 1)	MCHF (Ref. 6)	Perturbation (Ref. 8)	Present
1^1S	$\langle 1/r \rangle$	1.688 317	1.688 17	1.168 85	1.688 271
	$\langle r \rangle$	0.929 472	0.929 57	0.929 5	0.929 452
	$\langle r^2 \rangle$	1.193 483	1.193 76	1.192 5	1.193 196
2^1S	$\langle 1/r \rangle$		1.135 38	1.135 5	1.135 386
	$\langle r \rangle$	2.973 061	2.974 65	2.974	2.973 276
	$\langle r^2 \rangle$	16.089 24	16.108 47	16.10	16.087 96
2^3S	$\langle 1/r \rangle$	1.154 664	1.154 657	1.154 5	1.154 663
	$\langle r \rangle$	2.550 463	2.550 59	2.550 5	2.550 479
	$\langle r^2 \rangle$	11.464 32	11.465 6	11.465	11.464 41
2^1P	$\langle 1/r \rangle$	1.123 178	1.123 09	1.123	1.123 160
	$\langle r \rangle$	2.910 684	2.912 87	2.912	2.911 076
	$\langle r^2 \rangle$	15.765 65	15.790 0	15.775	15.769 58
2^3P	$\langle 1/r \rangle$	1.133 242	1.133 17	1.133 5	1.133 239
	$\langle r \rangle$	2.673 962	2.675 63	2.674	2.673 975
	$\langle r^2 \rangle$	13.211 74	13.229 9	13.21	13.210 65
3^1D	$\langle 1/r \rangle$				1.055 630
	$\langle r \rangle$				5.615 658
	$\langle r^2 \rangle$				63.163 67
3^3D	$\langle 1/r \rangle$				1.055 639
	$\langle r \rangle$				5.612 972
	$\langle r^2 \rangle$				63.109 06

TABLE IV. Mass-polarization effect for helium (in cm^{-1}).[a]

State	Pekeris *et al.* (Ref. 1)	Araki *et al.* (Ref. 11)	Machacek *et al.* (Ref. 12)	Present
1^1S	4.785			4.7960
2^1S	0.2859			0.2833
2^3S	0.2239			0.2233
2^1P	1.3852	1.3875	1.383[b]	1.3828
2^3P	-1.9426	-1.9445	-1.942[b]	-1.9424
3^1D				-0.7599×10^{-2}
3^3D				0.8027×10^{-3}

[a] $(2m/M)R=30.083\,87$ for ^4He is used to convert the present values of $\langle \vec{p}_1\cdot\vec{p}_2\rangle$ to $(1/m_n)\langle\vec{p}_1\cdot\vec{p}_2\rangle$ in cm^{-1}. See Schiff *et al.*, Ref. 1.

[b] As quoted in Schiff *et al.*, Ref. 1.

$$f_l=\frac{2}{3}\frac{(E_f-E_i)}{(2L+1)}\,|\langle\psi_f(L',0)\,|\,z_1+z_2\,|\,\psi_i(L,0)\rangle|^2\Big/\begin{bmatrix}L & 1 & L'\\ 0 & 0 & 0\end{bmatrix}^2 , \tag{7}$$

$$f_v=\frac{2}{3}\frac{1}{(E_f-E_i)(2L+1)}\left|\left\langle\psi_f(L',0)\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|\psi_i(L,0)\right\rangle\right|^2\Big/\begin{bmatrix}L & 1 & L'\\ 0 & 0 & 0\end{bmatrix}^2 . \tag{8}$$

TABLE V. The oscillator strengths between the lower-bound states of helium (f_l from dipole-length formula, and f_v from dipole-velocity formula).

Transition		Perimetric (Ref. 14)	Hylleraas (Ref. 2)	C.I. (Ref. 15)	MCHF (Ref. 6)	Perturbation expansion (Ref. 16)	Present
$1^1S\to2^1P$	f_l	0.2762	0.2759	0.275 4	0.2753	0.2760	0.272 1
	f_v	0.2762	0.2761	0.275 9	0.2744	0.2749	0.275 8
$2^1S\to2^1P$	f_l	0.3764	0.3764	0.377 3	0.3771	0.3764	0.376 1
	f_v	0.3764	0.3774	0.395 0	0.3774	0.3745	0.376 3
$2^3S\to2^3P$	f_l	0.5391	0.5391	0.539 8	0.5394	0.5392	0.539 2
	f_v	0.5391	0.5401	0.548 7	0.5400	0.5394	0.539 4
$2^1P\to3^1D$	f_l		0.7064	0.710 59	0.7111	0.7105	0.709 87
	f_v		0.7148	0.709 49	0.7105	0.7060	0.709 78
$2^3P\to3^3D$	f_l		0.6084	0.610 5	0.6115	0.6103	0.608 96
	f_v		0.6121	0.626 9	0.6099	0.6081	0.610 14

where $\begin{pmatrix} L & 1 & L' \\ 0 & 0 & 0 \end{pmatrix}$ is a $3j$ symbol.[13]

These two formulas for the oscillator strength would give identical results if exact wave functions were used. The use of approximate wave functions can produce differences in the two results. The agreement between the two formulas is a necessary condition for the accuracy of the two wave functions, but is not in itself sufficient to claim the accuracy of the wave functions.

The present results for the oscillator strengths from Eqs. (7) and (8) are given in Table V along with the results from Refs. 2 and 6, and those of Schiff *et al.*,[14] Green *et al.*,[15] and Divine and Stewart.[16] It is seen that the present results for the length and velocity formulas agree very well in most cases, the largest discrepancy being for the $1^1S \rightarrow 2^1P$ transition, where the disagreement is about 1% which is probably an indication that our ground-state wave function is comparatively poorer. For the $2^1S \rightarrow 2^1P$ and $2^3S \rightarrow 2^3P$ transitions the present results compare very favorably with those of Ref. 1, in comparison with the other calculations. It has been remarked in Ref. 14 that for triplet transitions the length formula does a better job, whereas for singlet transitions, even in the case where the transition is between two states with a small energy difference, the velocity formula does a better job.[14] Our results clearly support this argument. The agreement of the length and velocity formulas for the transitions $2^1P \rightarrow 3^1D$ and $2^3P \rightarrow 3^3D$ in the present work is significantly better than those of the other calculations.

SUMMARY

We have calculated the energies, radial expectation values, oscillator strengths, and mass-polarization effect of helium with configuration-interaction basis functions. These results are compared with other highly accurate results, where the coordinate r_{12} is explicitly used. We show more convincingly than before that while r_{12} is very important in obtaining a highly accurate result for the ground state, it is comparatively less important for excited states, especially for higher angular momentum states. For the $1s\,3d\;^{3,1}D$ states our results from the simpler basis functions give the same energy as the Hylleraas wave function, but our consistency between the oscillator strengths from the dipole-length and dipole-velocity formulas is much better. One would expect that the excited states of a many-electron system can be accurately calculated by these basis functions as well.

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