

2¹S states of the helium isoelectronic sequence

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We propose a simple analytic wave function for the 1s2s ¹S state of the two-electron atomic system. This is orthogonal to the ground-state function of Morse *et al.* The wave-function parameters are evaluated by the method of variational calculation for the eigenenergy. Using the present 2¹S-state function we have calculated the values of the physical quantities mean square radius and scattering cross section in a few cases. We compare these with the relevant values that are available using many-parameter wave functions and obtain good agreement.

I. INTRODUCTION

The wave functions of helium and a number of heliumlike ions in the 2S and 2P levels of both singlet and triplet multiplicity were given many years ago by Morse *et al.*¹ The formal simplicity of these state functions readily introduces an enormous calculational convenience in the theoretical determination of atomic properties. However, the 2¹S-state wave function of Morse *et al.* does not satisfy the condition of orthogonality with the ground-state function, thereby making it undesirable for use in calculation for scattering processes in general. The function is particularly unsuitable for use when a collision with a heliumlike atomic target results in a transition along the direct channel of scattering between the ground and 2¹S states of the target. Incidentally, Das *et al.*² have found in the course of their study of the electron-collisional excitation of heliumlike ions that the use of the nonorthogonal set of 1¹S- and 2¹S-state functions suggested by Morse *et al.* is not justified. In such a case calculation with and without retention of the electron-nucleus interaction term yields in the Coulomb-Born approximation² cross section values of different orders for the 1¹S→2¹S transition in the particular two-electron system Li⁺. In fact, the fulfillment of the condition of mutual orthogonality by the initial and final target-state functions is here truly essential, since the mere addition of a constant to the potential would otherwise change the cross section value. With this in view we have proceeded to develop for the two-electron atomic system a suitable 2¹S-state function which we think remedies the inadequacy found for this state in the wave function of Morse *et al.*

II. THEORY

The construction of our singlet S-state wave function for an atomic system having two electrons, a

1s and a 2s, is based upon the consideration that the two orbitals assumed in the expressions

$$\begin{aligned} u_{1s}(r) &= M(4\pi)^{-1/2}e^{-Zr}, \\ u_{2s}(r) &= N(4\pi)^{-1/2}(e^{-\beta r} - Sre^{-\nu r}) \end{aligned} \quad (1)$$

are not mutually orthogonal. Instead the orthogonality of the total 2¹S-state function (normalized)

$$\begin{aligned} \Psi_{2^1S}(\vec{r}_1, \vec{r}_2) &= [2(1 + \Delta^2)]^{-1/2} \\ &\times [u_{1s}(r_1)u_{2s}(r_2) + u_{1s}(r_2)u_{2s}(r_1)] \end{aligned} \quad (2)$$

with the approximate ground-state function

$$\Psi_{1^1S}(\vec{r}_1, \vec{r}_2) = Z'^3\pi^{-1} \exp[-Z'(r_1 + r_2)] \quad (3)$$

is ensured, the latter being reported by Morse *et al.* The nuclear charge of the atomic system Z is related to Z' as $Z' = (Z - 1) + 0.69$. The normalizing factors M and N for the two orbitals are given by

$$M = 2Z^{3/2}, \quad N = [\frac{1}{4}\beta^{-3} - 12S(\beta + \nu)^{-4} + \frac{3}{4}S\nu^{-5}]^{-1/2}, \quad (4)$$

while S is fixed by the mutual orthogonality of Ψ_{2^1S} and Ψ_{1^1S} at

$$S = \frac{1}{3}(Z + \nu - 0.31)^4(Z + \beta - 0.31)^{-3}. \quad (5)$$

Lastly, Δ in Eq. (2) stands for the overlap integral between the 1s and 2s orbitals that build up our 2¹S wave function. The integral survives because the orbitals are not orthogonal, and works out to be

$$\Delta = 2MN[(Z + \beta)^{-3} - 3S(Z + \nu)^{-4}]. \quad (6)$$

In order to obtain the parameters β and ν , we carry out variational calculations for the eigenenergy

$$\epsilon = \int d\vec{r}_1 d\vec{r}_2 \Psi_{2^1S}^* H \Psi_{2^1S}(\vec{r}_1, \vec{r}_2), \quad (7)$$

H denoting the Hamiltonian of the system. For this we set $\delta\epsilon = 0$ and arrive in the process at a pair of nonlinear equations in β and ν :

$$f(\beta, \nu) = 0, \quad g(\beta, \nu) = 0. \quad (8)$$

These are solved for β and ν by the method of iteration as suggested by Newton.³

The primary requirement for such a solution³ is the knowledge of an approximate estimate of these quantities. Looking at the assumed form of our 2s orbital, we see that its asymptotic nature is indicated by the term involving ν , while the part of u_{2s} that contains β gives us an idea of the short-range behavior of the function. Thus the parameter β is likely to be the larger of the two. An initial estimate of ν can be made at $\frac{1}{2}(Z-1)$, if in the asymptotic region the 2s electron is considered completely screened by the inner 1s electron, so that the former lies in the field of an effective nuclear charge one less than the actual charge of the nucleus, i.e., $Z-1$. The parameter β may likewise be approximately set equal to $\frac{1}{2}Z$, if it is assumed that the 2s electron in the region near the nucleus realizes the field due to the whole nuclear charge Z .

With the estimate of β and ν obtained above, iteration is continued according to Newton's method until the magnitudes of the differential corrections³ $\delta\beta$ and $\delta\nu$ become negligible.

III. RESULTS AND DISCUSSION

Parameters have been computed for the He atom and for all like positive ions with Z less than or equal to ten. Table I presents the values of our parameters along with the eigenenergies they yield. The experimental eigenenergies are also included in the table for comparison.

As an additional test of convergency for He, it has been found that the use of the parameters derived by Marriott and Seaton⁴ as the input for our iterative procedure results in exactly those values given in Table I. But no convergence is attained when we employ the parameters of Morse *et al.*

for this purpose. The reason for this is probably that the value of β found by Morse *et al.* is much further from our value than that of Marriott and Seaton is, ν differing little in either case. In fact Newton's iterative method essentially seeks³ that the initial approximate solution be sufficiently close to the final one. Since convergence has very nearly been achieved in our calculation of wave-function parameters for all the two-electron atomic systems considered, our original estimates of β and ν prove quite reasonable in producing a solution of Eqs. (8).

The eigenenergies we found for the 2^1S states of the atomic systems under consideration are quite close to values obtained experimentally,⁵ as evidenced by Table I. The present parameters for He have been utilized to calculate⁴ the mean-square radius \bar{r}^2 and the square of the integral σ required for calculation of the threshold photoionization cross section. Table II clearly shows that our value of \bar{r}^2 agrees with that produced⁴ by the best Coolidge-James⁶ function for He 2^1S better than that determined by means of the wave function of Marriott and Seaton does. However, for $|\sigma|^2$, the present wave function is almost equivalent to the Marriott-Seaton function, though it leaves a small discrepancy with the yield of the Coolidge-James wave function (37.6 vs 40.2 a.u.).

Our wave functions for the 2^1S states of Li^+ , Be^{2+} , and O^{6+} are employed together with the 1^1S -state functions of Morse *et al.* to calculate² the Coulomb-Born cross sections for the electron-collisional 1^1S-2^1S excitations of the ions. These are compared in Table III with the corresponding cross sections obtained by Tully⁷ using the many-parameter wave functions of Cohen and McEachran^{8,9} and McEachran and Cohen¹⁰ at several incident-electron energies. It appears that our values of the cross sections are of the right order of magnitude, although they differ somewhat from the

TABLE I. 2^1S wave-function parameters and eigenenergies (a.u.) for He and like atomic systems.

Z	β	ν	$-\epsilon$ (calculated)	$-\epsilon$ (experimental) ^a
2.0	0.774 17	0.537 85	2.145 45	2.146 00
3.0	1.557 09	0.999 75	5.038 23	5.041 20
4.0	1.556 00	1.556 91	9.180 19	9.185 58
5.0	2.060 27	2.059 85	14.572 4	14.579 5
6.0	3.626 78	2.438 18	21.215 6	21.225 0
7.0	3.064 45	3.064 47	29.107 5	29.119 4
8.0	3.567 51	3.566 16	38.250 3	38.264 5
9.0	4.066 40	4.067 55	48.643 1	48.660 1
10.0	4.565 91	4.568 71	60.286 0	60.322 5

^aObtained by adding the experimental ionization energy,⁵ after conversion into atomic units, to $\frac{1}{2}Z^2$.

TABLE II. Values of $\overline{r^2}$ and $|\sigma|^2$ for He.

2 ¹ S wave function used	$\overline{r^2}$	$ \sigma ^2$
Morse <i>et al.</i>	21.7	9.6
Marriott and Seaton	38.8	37.2
Present	32.7	37.6
Coolidge and James	33.1	40.2

results based upon the use of the McEachran-Cohen wave functions. Quantitatively speaking, the ratio $\rho = P/MCN$ varies for O⁶⁺ from 0.700 at $X = 1.0$ to 0.898 at $X = 3.0$, with intermediate values of ρ for Li⁺ and Be²⁺.

IV. CONCLUSION

In general, there is always a need for such a simple 2¹S wave function as ours for use in a variety of calculations. To simplify such calculations it is often desirable to introduce relatively simple wave functions rather than those of Hartree and of Coolidge and James, or the other many-parameter wave functions suggested⁸⁻¹⁰ for a few members of the helium isoelectronic sequence. The wave functions we have developed for the singlet 2S states of the two-electron atomic

TABLE III. Coulomb-Born cross sections (πa_0^2) for the electron-impact 1¹S → 2¹S excitations of Li⁺, Be²⁺, and O⁶⁺.

	X^a	P^b	MCN^c
Li ⁺	1.0	1.33, -02 ^d	1.68, -02
	2.0	6.99, -03	9.34, -03
	3.0	4.76, -03	6.45, -03
Be ²⁺	1.0	4.16, -03	5.05, -03
	2.0	2.29, -03	2.82, -03
	3.0	1.56, -03	1.93, -03
O ⁶⁺	1.0 ^e	2.10, -04	3.00, -04
	2.0	1.42, -04	1.62, -04
	3.0	9.88, -05	1.10, -04

^a Incident-electron energy in threshold units.

^b Cross section determined by means of the present 2¹S wave function.

^c Cross section determined by means of the McEachran-Cohen wave function.

^d The number after the comma represents the power of ten by which the value should be multiplied.

^e In the preliminary set of results reported in Ref. 11, the threshold cross section for the ion O⁶⁺ was too low, and so seems inconsistent. This inconsistency has been found to have originated in the computation course for O⁶⁺, and the corrected threshold cross section value is given in this table.

systems are expected to serve this purpose in view of the fact that they have produced fairly good results for He, Li⁺, Be²⁺, and O⁶⁺.

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