PHYSICAL REVIEW A VOLUME 51, NUMBER 3 MARCH 1995

Double photoionization of excited ^1S and ^3S states of the helium isoelectronic sequence

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(Received 12 August 1994; revised manuscript received 14 October 1994)

We present results for the photoionization of ground and excited S states of two-electron systems by x-ray photons. The method uses the asymptotic formulation of Dalgarno and Stewart [Proc. Phys. Soc. London **76**, 49 (1960)] with highly correlated Frankowski-Pekeris–type wave functions for $N\,^1S$ and $N\,^3S$ initial states. The calculations show a smaller ratio of double-to-single photoionization R for triplet states due to the spatial antisymmetry of the wave function near the nucleus. We find an asymmetric population of photoion satellite states and provide expressions for the asymptotic single and total photoionization, and R as a function of nuclear charge. We also make predictions for the differential double photoionization cross sections in the extreme energy sharing case when one electron is ejected with zero energy.

PACS number(s): 32.80.Fb, 32.30.Rj, 32.70.Cs

I. INTRODUCTION

Considerable attention has been given recently in experimental [1–3] and theoretical [4–8] studies to the double ionization of the ground state of helium by the absorption of a high-frequency photon. The double photoionization (DPI) of the other members of the helium sequence and of the metastable $2\,^3S$ states of helium have also been investigated [5,9,10]. It has been established that the ratio of the double-to-single photoionization cross section tends to a constant at high frequencies. The asymptotic ratio can be calculated accurately in the acceleration form of the electric-dipole operator, provided that electron-electron correlation is adequately represented in the initial state wave function [11].

In this paper, we employ fully correlated initial state wave functions for the ground and excited ^1S and ^3S states of helium to predict the asymptotic ratios for single and double photoionization. We use an extrapolation of the simultaneous excitation and ionization cross sections in the double-ionization limit to obtain the differential cross section for double photoionization in which one electron is ejected with zero energy. To explore further the role of electron-electron correlation, we investigate the dependence of the ratios and cross sections on the nuclear charge Z.

II. THEORY

A. Asymptotic formulation

The fundamental physical quantity in the photoexcitation-ionization process

$$\hbar\omega + \mathrm{He}(N\,^{1,3}S) \rightarrow \mathrm{He}^+(ns) + e^- \tag{1}$$

is the continuum dipole oscillator strength

$$\frac{df_n}{d\epsilon} = 2\omega |\langle \psi_n(\vec{r}_1,\vec{r}_2)|\hat{\lambda}\cdot\vec{d}\,|\Psi(\vec{r}_1,\vec{r}_2)\rangle|^2 , \tag{2}$$

where ω and ϵ are the respective energies of the photon and ionized electron in atomic units and $\hat{\lambda}$ is the direction of linearly polarized light. $\Psi(\vec{r}_1,\vec{r}_2)$ represents a fully correlated initial state wave function, which is denoted by $\Psi(r_1,r_2,r_{12})$ for S states, and $\psi_n(\vec{r}_1,\vec{r}_2)$ is the final state product wave function for a continuum electron and a hydrogenic s-state electron with principle quantum number n. The coordinates r_1 and r_2 are the electronic distances from the nucleus, and r_{12} is the interelectronic distance. By Fourier transforming the acceleration form of the electric-dipole operator

$$\vec{d} = \frac{Z}{\omega^2}\left[\frac{\vec{r}_1}{r_1^3} + \frac{\vec{r}_2}{r_2^3}\right] , \tag{3}$$

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it was shown [11] that

$$\frac{df_n}{d\epsilon} \sim C(ns)(2\epsilon)^{-7/2} \quad (\epsilon \to \infty)\ , \tag{4}$$

where

$$C(ns) = \frac{512\pi Z^2}{3} \left| \int_0^\infty r_1^2 dr_1 \Psi(r_1,0,r_1) u_{ns}(r_1) \right|^2 , \tag{5}$$

with $u_{ns}(r)$ the final hydrogenic s-state wave function. Hydrogenic states of higher angular momentum are known [5] to contribute an additional factor of ϵ^{-l} to the expansion (4) and can, therefore, be neglected.

The asymptotic ratio of double-to-single ionization cross section is defined by

$$R = \frac{C}{\sum_n C(ns)} - 1\ , \tag{6}$$

where the constant C is the sum of all $C(ns)$ contributions including double ionization such that the total photoabsorption cross section at high energy behaves as

$$\sigma_{\mathrm{tot}} = \frac{2\pi^2}{137} C(2\epsilon)^{-7/2}\ . \tag{7}$$

Using (5) and the closure relation for hydrogenic eigenstates, it was shown [11] that

$$C = \frac{512\pi Z^2}{3} \int_0^\infty r_1^2 dr_1 |\Psi(r_1,0,r_1)|^2\ . \tag{8}$$

The physical manifestation of the above DPI process is as follows. At high photon energies, the photoionization volume about the nucleus shrinks to a small sphere of radius $r \sim k^{-1}$, where k is the photon momentum transfer. This "shrinking volume" effect causes the two-electron wave function to collapse onto the nucleus, releasing a photoelectron with nearly all of the photon energy and angular momentum. The remaining electron leaves with very little escape energy and zero angular momentum.

B. Initial state wave function

For the fully correlated initial state wave function, we use a finite basis set of Frankowski-Pekeris–type functions [12,13]

$$\phi_{nlmj}(s,t,u) = s^n t^l u^m (\ln s)^j \exp(-s/2) \begin{Bmatrix} \cosh(ct) \\ \sinh(ct) \end{Bmatrix} \tag{9}$$

in the Hylleraas coordinates

$$s = r_1 + r_2\ , \quad t = r_2 - r_1\ , \quad u = r_{12}\ ,$$

subject to the constraints

$$l, m \geq 0$$

and

$$(n + l + m) \geq \begin{cases} 2j \geq 0 & \text{if } n \geq 0 \\ 2j + 2 \geq 0 & \text{if } n < 0\ . \end{cases}$$

This basis set provides the correct cusp structure at all two-particle coalescences due to linear terms in r_1, r_2, and r_{12} and the correct singularity structure at the three-particle coalescence since the logarithmic terms of the Fock expansion [14–18] are expandable in powers of s, $\ln(s)$, and (t/s). For the ground state, the nonlinear variational parameter c is zero, and we require that l be even in order to ensure that the basis set has the proper symmetry under exchange of particles $r_1 \leftrightarrow r_2$, or equivalently, $t \leftrightarrow -t$. For excited states, c is used to build in the radial "in-out" correlation in which one electron is close to the nucleus with the other electron far away. The choice of $\cosh(ct)$ or $\sinh(ct)$ is made to give the basis function the proper symmetry under exchange of particles. Hence, for singlet states $\cosh(ct)$ is used when the index l is even and $\sinh(ct)$ is used with odd values of l. For triplet states, the situation is reversed.

In general, the initial state wave function is expanded as a sum of scaled Frankowski-Pekeris functions (9)

$$\Psi(r_1,r_2,r_{12}) = \sum_{klmj} c_{klmj} \phi_{klmj}(as,at,au)\ . \tag{10}$$

Substituting (10) into (5) and (8), we obtain

$$C(ns) = \frac{16a^6 Z^2}{3\pi} \left\{ \sum_{klmj} c_{klmj} (-1)^l \int_0^\infty r_1^2 dr_1 (ar_1)^{k+l+m} [\ln(ar_1)]^j \times u_{ns}(r_1) [\exp(-\alpha r_1) + (-1)^{l+S} \exp(-\beta r_1)] \right\}^2 \tag{11}$$

and

$$C = \frac{16a^6 Z^2}{3\pi} \sum_{klmj} \sum_{k'l'm'j'} c_{klmj} c_{k'l'm'j'} (-1)^L \int_0^\infty r_1^2 dr_1 (ar_1)^{K+L+M} [\ln(ar_1)]^J \times [\exp(-\alpha r_1) + (-1)^{l+S} \exp(-\beta r_1)] \times [\exp(-\alpha r_1) + (-1)^{l'+S} \exp(-\beta r_1)]\ , \tag{12}$$

TABLE I. Energy eigenvalue E and constant C for helium S states.

	$N\,^1S$		$N\,^3S$	
N	E	C	E	C
1	$-2.903\,724\,377\,034$	309.0		
2	$-2.145\,974\,046\,054$	223.5	$-2.175\,229\,378\,236$	225.3
3	$-2.061\,271\,989\,738$	219.0	$-2.068\,689\,067\,472$	219.3
4	$-2.033\,586\,716\,953$	218.0	$-2.036\,512\,083\,096$	218.1

where $\alpha=a(\frac{1}{2}+c)$ and $\beta=a(\frac{1}{2}-c)$. Here $K=k+k'$, $L=l+l'$, $M=m+m'$, and $J=j+j'$. As usual, $S=0$ for singlet states and $S=1$ for triple states. The normalization of the wave function combines with the constant in (5) and (8) to yield $16a^6Z^2/(3\pi)$.

III. RESULTS

Table I gives the energy eigenvalues of the low-lying S states of helium studied in this work. The binding energies agree with the results of Drake [19] to an accuracy of ten digits or better, so we expect that the wave functions are accurate to five digits. Included in Table I is the constant C calculated from Eq. (3).

The ratio of asymptotic oscillator strengths $C(ns)/C$ and the ratio R of double-to-single photoionization for helium S states are shown in Table II. We find that R is larger for singlet states than for triplet states of the same level. This is due to the shrinking volume effect with its dependence on the wave function at the nucleus [5]. Since singlet state wave functions of natural parity (which include all singly excited states) do not vanish as both electrons approach the nucleus [20], while triplet state wave functions do vanish there because they are spatially antisymmetric and continuous, the probability for photoabsorption, and hence the ratio of double-to-single photoionization, is largest from the singlet states of natural parity. Following the discussion of Morgan and Kutzelnigg [20], we would expect that metastable doubly excited singlet states of unnatural parity, whose wave functions vanish even faster than those of triplet states as both electrons approach the nucleus, would show still smaller double-to-single photoionization ratios than the corresponding triplet states.

Table II also shows an interesting feature of single ionization—the asymmetric population of satellite $\mathrm{He}^+(ns)$ states. It is particularly illustrative to consider this concept in the framework of the hyperspherical coordinates method [21,22]. In this picture, different excitation continua are populated via direct vertical dipole transition to the repulsive parts of the adiabatic hyperspherical potential energy curves. For the ground state, this continuum is mainly the $1s\epsilon p$ continuum. For the $2\,^1S$ state, the most readily available continua, having the largest overlaps with the initial state, are $2s\epsilon p$ and $3s\epsilon p$ continua, not the $1s\epsilon p$ continuum. This type of vertical Franck-Condon bound-continuum transition persists in populating the satellite states of He^+ states shown in Table II. The effect becomes more pronounced for the higher excited initial states. For instance, in the high-frequency photoionization of the $4\,^1S$ state of helium, $\mathrm{He}^+(n=5)$ is produced with the highest probability.

The values of the ratio R for the ground and metastable states of the helium isoelectronic sequence from $Z=1$ to $Z=10$ are presented in Table III. The variation of R with Z is illustrated in Fig. 1. Kornberg and Miraglia [23] have shown that the double-photoionization cross sections diminish as Z^{-4} for large Z and the ratio R diminishes as Z^{-2}. Our values of R (expressed in percent) behave for large Z as

$$R\sim\frac{9}{Z^2}-\frac{3}{Z^3} \tag{13}$$

for the $1\,^1S$ states,

$$R\sim\frac{32}{Z^2}-\frac{66}{Z^3} \tag{14}$$

for the $2\,^1S$ states, and

$$R\sim\frac{6}{Z^2}-\frac{9}{Z^3} \tag{15}$$

for the $2\,^3S$ states.

The ratios of the $2\,^1S$ states exceed those of the $1\,^1S$

TABLE II. Ratios $C(ns)/C$ and R for helium S states.

n	$1\,^1S$	$2\,^1S$	$2\,^3S$	$3\,^1S$	$3\,^3S$	$4\,^1S$	$4\,^3S$
1	0.9296	0.0493	0.0338	0.0136	0.0087	0.0055	0.0034
2	0.0446	0.5346	0.7824	0.0702	0.0591	0.0232	0.0170
3	0.0055	0.3993	0.1733	0.1669	0.4054	0.0534	0.0903
4	0.0018	0.0035	0.0044	0.7318	0.5230	0.0019	0.0761
5	0.0008	0.0017	0.0014	0.0131	0.0006	0.7768	0.7595
6	0.0005	0.0009	0.0006	0.0001	0.0004	0.1372	0.0524
7	0.0003	0.0005	0.0003	0.0001	0.0003	0.0003	0.0001
≥ 8	0.0008	0.0013	0.0008	0.0005	0.0007	0.0001	0.0002
R (%)	1.644	0.9033	0.3118	0.3691	0.1967	0.1682	0.1042

TABLE III. Z dependence of R (%).

Z	$1\,^1S$	$2\,^1S$	$2\,^3S$
1	1.602		
2	1.644	0.903	0.312
3	0.856	1.204	0.304
4	0.508	0.995	0.222
5	0.334	0.768	0.162
6	0.236	0.595	0.121
7	0.175	0.469	0.093
8	0.135	0.378	0.074
9	0.107	0.309	0.060
10	0.087	0.258	0.050

states for $Z > 3$ despite the fact that the metastable states are less localized near the nucleus. The same feature occurs for the $3\,^1S$ states. Figure 2 shows the variation with Z of $C(ns)$ for the $1\,^1S$, $2\,^1S$, and $2\,^3S$ states for several values of n. For the $1\,^1S$ states, the ratio of asymptotic oscillator strengths $C(ns)/C$ is concentrated in $C(1s)/C$ and it converges quickly toward its large-Z asymptotic value of

$$\frac{C(1s)}{C} \to \frac{|u_{1s}(0)|^2}{|u_{1s}(0)|^2} = 1 , \tag{16}$$

which is obtained by ignoring the electron-electron interaction. Photoionization from the $2\,^1S$ and $2\,^3S$ states, however, can populate the $\mathrm{He}^+(1s)$ and $\mathrm{He}^+(2s)$ states, as shown in Fig. 2. The $2\,^1S$ and $2\,^3S$ large-Z asymptotic limits

$$\frac{C(1s)}{C} \to \frac{|u_{2s}(0)|^2}{|u_{1s}(0)|^2 + |u_{2s}(0)|^2} = \frac{1}{9} \tag{17}$$

$$\frac{C(2s)}{C} \to \frac{|u_{1s}(0)|^2}{|u_{1s}(0)|^2 + |u_{2s}(0)|^2} = \frac{8}{9} , \tag{18}$$

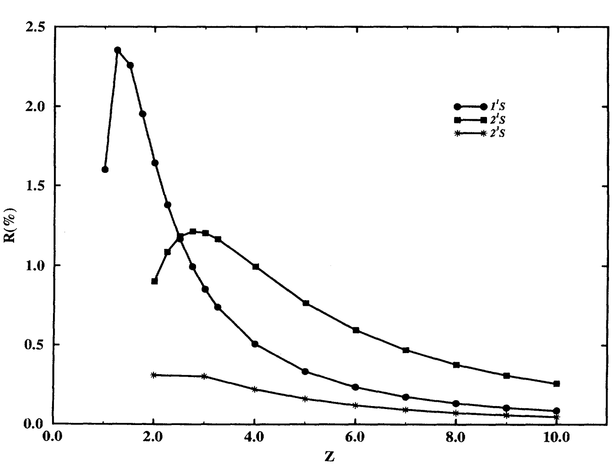

FIG. 1. Ratio of double-to-single photoionization for the $1\,^1S$, $2\,^1S$, and $2\,^3S$ states of the helium isoelectronic sequence.

are approached more slowly than the $1\,^1S$ large-Z asymptotic limit, probably due to the additive nature of the population of different $C(ns)/C$ states as the two-electron wave functions are progressively localized to regions of space near the nucleus, i.e., size $\sim 1/Z$. In gen-

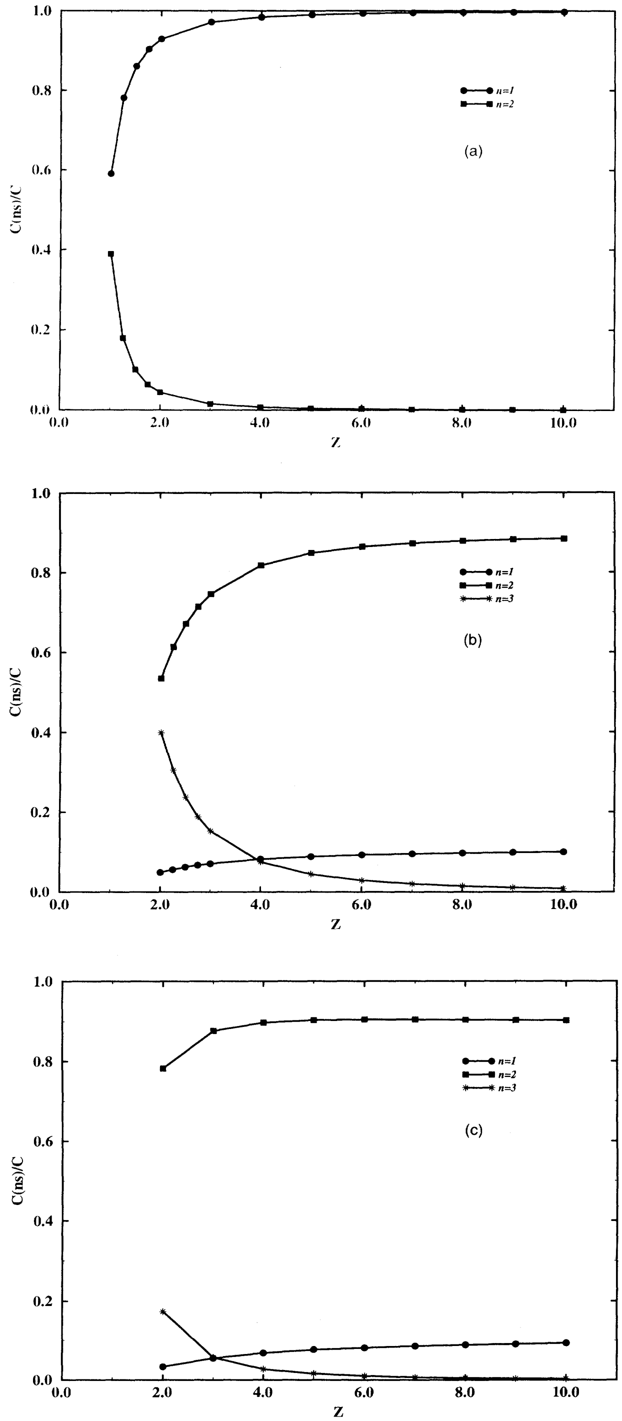

FIG. 2. Ratio of asymptotic oscillator strengths for the $1\,^1S$, $2\,^1S$, and $2\,^3S$ states of the helium isoelectronic sequence in (a), (b), and (c), respectively. Each curve approaches its asymptotic value given in the text.

TABLE IV. Fitting parameters M and σ in Eqs. (19) and (20).

State	M	M_1	M_2	σ	σ_1	σ_2
$1\,^1S$	13.6	13.6		0.136	0.141	
$2\,^1S$	7.6	0.85	6.8	0.037	0.241	0.062
$2\,^3S$	7.6	0.85	6.8	0.027	0.384	0.011

eral, the Z dependence of $C(ns)$ and C can be fitted to the forms

$$C(ns)=M_n(Z-\sigma_n)^5 \tag{19}$$

and

$$C=M(Z-\sigma)^5 , \tag{20}$$

where the parameters M and σ are tabulated in Table IV. The ratios M_n/M equal the large-Z limits in Eqs. (16)–(18), while the screening parameters σ characterize the electron-electron correlation.

We may, following the procedures of Fan, Sadeghpour, and Dalgarno [24], obtain the asymptotic values of the zero energy differential cross sections for double photoionization in which one of the electrons is ejected with zero energy. We use the formula

$$\left.\frac{d\sigma^{2+}}{d\epsilon'}\right|_{\epsilon'=0}=\frac{2\pi^2}{137}Q(Z)(2\epsilon)^{-7/2} , \tag{21}$$

where ϵ is equal to the photon energy minus the ionization potential, and

$$Q(Z)=\lim_{n\to\infty} n^3C(ns) . \tag{22}$$

Table V shows our extrapolated values of $Q(Z)$ for the $1\,^1S$, $2\,^1S$, and $2\,^3S$ states; for He($1\,^1S$), $Q(Z=2)$ is 27, 14% larger than the value obtained by Fan, Sadeghpour, and Dalgarno [24] with a less accurate representation of the initial wave function.

In summary, we show results for the DPI of the ground and excited states of the helium isoelectronic sequence in the asymptotic photon energy limit. Using fully correlated initial state wave functions, we find a smaller ratio of double-to-single photoionization for triplet states than for singlet states of the same level. The Z dependence of the ratio R shows a maximum that depends on the initial state of the system. This is related to the excitation of asymmetric satellite states of $\mathrm{He}^+(n)$ and its isoelectronic partners during the photoionization process. It is shown that the ratios R have simple large-Z dependences, which are in agreement with a recent calculation [23]. We also show that the asymptotic single and total photoionization cross sections have simple Z-scaling properties and give predictions for the differential DPI cross sections in the extreme energy sharing case.

TABLE V. $Q(Z)$ vs Z in Eq. (22).

Z	$1\,^1S$	$2\,^1S$	$2\,^3S$
2	27	29	17
3	107	350	130
4	266	121 0	391
5	533	280 0	849
6	934	530 4	1558
7	1494	891 8	2564
8	2244	138 34	3927
9	3210	202 46	5695
10	4417	283 48	7918

ACKNOWLEDGMENTS

The work of A.D. and H.R.S. was supported by the U.S. Department of Energy, Division of Chemical Sciences, office of Basic Energy Sciences, Office of Energy Research. The work of J.D.B. and J.D.M. was supported by NSF Grant No. PHY-9215442. J.D.B. and J.D.M. greatly appreciate the hospitality of the Department of Chemistry at Harvard University extended by Dudley Herschbach and members of his group. R.C.F. gratefully acknowledges Robert Nyden Hill and Ramesh Sharma for helpful insights and financial support.

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