Wavelength dependence of the nonresonant photoionization cross section of a two-electron atom near the ionization threshold

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(Received 28 November 1994)

We present the theoretical near-threshold photoionization cross sections of He atoms from bound excited states, using a *B*-spline-based configuration-interaction method. Our study has shown that in the absence of a strongly energy-dependent feature such as a doubly excited resonance, the photoionization cross sections in the immediate vicinity of the ionization threshold depend *linearly* on the wavelengths of the incident light. Qualitatively, following the quantum-defect theory, this linear dependence can be linked directly to the expected nearly energy-independent scattering phase shift corresponding to the wave function of the ionized electron at near-zero photoelectron energy.

PACS number(s): 32.80.Fb, 31.50.+w, 31.25.Jf, 31.15.Ar

I. INTRODUCTION

In spite of an agreement on the absolute cross section within the experimental uncertainty between our recent theoretical calculation [1] and the earlier experiment [2] on the He photoionization from the $1s2s\ ^{1,3}S$ states, our theory was unable to confirm the experimental observation that the $1s2s\ ^1S$ cross section nearly equals the $1s2s\ ^3S$ cross section at energies close to the $1s2s\ ^3S$ ionization threshold. In particular, our numerical calculation has shown that not only the ratio R between the $1s2s\ ^1S$ and the $1s2s\ ^3S$ photoionization cross sections varies noticeably as a function of the wavelength, the values of R also deviate significantly from the unity at energies close to the $1s2s\ ^3S$ threshold. In this paper, additional theoretical considerations are presented to support our earlier conclusion that the ratio R near the $1s2s\ ^3S$ ionization threshold should deviate from a constant value.

We will first show theoretically that, in the absence of a strongly energy-dependent feature such as a doubly excited resonance, the photoionization cross sections at energies very close to the ionization threshold follow a *linear* wavelength dependence. For the He atom, the $1s2s\ ^1S$ and $1s2s\ ^3S$ ionization thresholds are separated by approximately 520 Å (i.e., 3121.8 and 2600.6 Å for ^1S and ^3S, respectively) and, consequently, the ratio R at wavelengths close to the He $1s2s\ ^3S$ threshold (e.g., between 2600 and 2400 Å) cannot be a constant since the $1s2s\ ^1S$ photoionization cross sections are no longer, whereas the $1s2s\ ^3S$ cross sections remain, being linearly dependent upon the wavelengths. To further support our conclusion, the detailed theoretical cross sections based on *B*-spline-based configuration-interaction (BSCI) calculation [3,4] on photoionization from bound excited $^{1,3}S$ and $^{1,3}P$ states with photon energies up to approximately 0.1 eV above their respective ionization thresholds are also presented.

II. THEORY

The photoionization cross sections (in unit of a_0^2) from an initial state $|I\rangle$ to a final state $|E\rangle$ in a single ionized continuum are given theoretically by [3,4]

$$\sigma=\frac{8}{3}\pi^2\alpha g(E_\gamma)|D_{EI}|^2\ , \tag{1}$$

where E_γ is the photon energy given in atomic unit, α is the fine-structure constant, and $g(E)=E$ and E^{-1} for the dipole length and velocity approximations, respectively. The dipole matrix D_{EI} is given by

$$D_{EI}=\langle\Phi_E^{\Lambda'}|\hat{D}|\Phi_I^{\Lambda}\rangle\ , \tag{2}$$

where $\hat{D}$ is the dipole operator and Φ_I^Λ and $\Phi_E^{\Lambda'}$ are the state wave functions of the initial and final states. The symmetries of the initial and final states, each identified by a set of angular momentum quantum numbers in the LS coupling, are denoted by Λ and Λ', respectively [3,4].

If the initial state $|I\rangle$ of the photoionization is not strongly correlated, its state function Φ_I^Λ, calculated in the BSCI procedure for a two-electron or a divalent atom [3,4], is dominated by a single configuration series in terms of its corresponding configuration series function $\Xi^\Lambda_{E,\mu ll'}$, e.g., the $1ss$ series in terms of $\Xi^\Lambda_{E,1ss}$ for He $1sns\ ^{1,3}S$ states. Similarly, in the absence of doubly excited resonance, the final-state continuum is also dominated by a single configuration series function, e.g., $\Xi^\Lambda_{E,1sp}$ for the $1s\epsilon p\ ^{1,3}P$ continua. As a result, qualitatively, the near-threshold nonresonant $1sns\ ^{1,3}S\rightarrow 1s\epsilon p\ ^{1,3}P$ photoionization of He is dominated by the $ns\rightarrow\epsilon p$ one-electron transition. Following the BSCI approach, the ionized electron, i.e., the outer electron occupying the ns and ϵp orbitals in its respective initial and final states, is represented by the effective one-electron functions ξ_{ns} and $\xi_{\epsilon p}$ defined by equations similar to Eq. (10) in Ref. [3], i.e.,

$$\xi_{ns}(r)=\sum_{\nu} C^{\Lambda}_{1sns\ ^{1,3}S}(1s,\nu s)\chi_{\nu s}(r) \tag{3}$$

and

$$\xi_{\epsilon p}(r)=\sum_{\nu} C^{\Lambda}_{E}(1s,\nu p)\chi_{\nu p}(r)\ , \tag{4}$$

where $\chi_{\nu l}$ is a nearly complete set of discretized B-spline-based hydrogenic functions and $C^{\Lambda}(1s,\nu l)$ represents a set of coefficients in the state function corresponding to the $1sl$ configuration series. The kinetic energy ϵ and the momentum k of the outgoing photoelectron are given by $\epsilon=k^2/2=E+E_I$, where E is the total energy measured from the double-ionization threshold in the BSCI approach and E_I is the ionization energy of the remaining $1s$ electron of the He^+ ion. Qualitatively, for the nonresonant $1sns\ ^{1,3}S\rightarrow 1s\epsilon p\ ^{1,3}P$ photoionization, the dipole matrix D_{EI} is dominated by a one-particle radial matrix

$$d_{\epsilon i}=\langle \rho_{\epsilon p}|d|\xi_{ns}\rangle\ , \tag{5}$$

where d is the radial dipole operator and

$$\rho_{\epsilon l}(r)=\frac{1}{A}\left[\frac{2}{\pi k}\right]^{1/2}\xi_{\epsilon l}(r) \tag{6}$$

is normalized asymptotically according to the expression [3]

$$\left[\frac{2}{\pi k}\right]^{1/2}\sin\left[kr+\frac{q}{k}\ln(2kr)-\frac{l\pi}{2}+\delta_C+\delta_l\right] \quad \text{as } r\rightarrow\infty\ , \tag{7}$$

where A is the amplitude of the oscillating function $\xi_{\epsilon l}$ at large r, q is the effective nuclear charge experienced by the outgoing photoelectron, and δ_C and δ_l are the Coulomb and scattering phase shifts, respectively.

The radial functions ξ_{ns} corresponding to the $1s2s\ ^{1,3}S$ and $1s3s\ ^{1,3}S$ initial states are shown in Fig. 1. As expected, ξ_{ns} extends approximately to a distance $r_c\sim 2\langle r_c\rangle$, or $3\nu^2/q$, where ν is the corresponding effective principal quantum number. If the photoelectron energy k^2 is substantially smaller than the Coulomb interaction $2q/r_c$, or

$$k^2 \ll \frac{2}{3}\frac{q^2}{\nu^2}\ , \tag{8}$$

the radial $\rho_{\epsilon p}$, which effectively represent the oscillating part of the outgoing electron in the continuum, should be nearly independent of k up to r_c. In fact, the lack of energy dependence in $\rho_{\epsilon p}$ at small r, or, equivalently, a nearly energy-independent scattering phase shift, is expected from quantum-defect theory as the nearly constant quantum defect of the highly excited Rydberg state extends across the ionization threshold. This is clearly illustrated in Fig. 1, where a few selected $\rho_{\epsilon p}$ at momenta close to the ionization threshold are shown to be essentially indistinguishable up to r_c. As a result, the dipole matrix $d_{\epsilon i}$, calculated in the velocity approximation, should also be independent of the energy. Together with the E^{-1} energy dependence from Eq. (1), it can be concluded readily that the near-threshold photoionization cross section is *linearly* dependent upon the wavelength λ of the incident photon in the dipole velocity approximation. As for the dipole length approximation, the small difference in $\rho_{\epsilon p}$ is amplified by the operator r at a larger distance. As expected, our calculation has shown that the dipole matrix $d_{\epsilon i}$ in the length approximation increases as a function of λ, leading to a cross section that is also linearly proportional to λ. In the dipole acceleration approximation, the radial matrix $d_{\epsilon i}=\langle \rho_{\epsilon p}|1/r^2|\xi_{ns}\rangle$ is also energy independent. This appears to suggest a λ^3 dependence

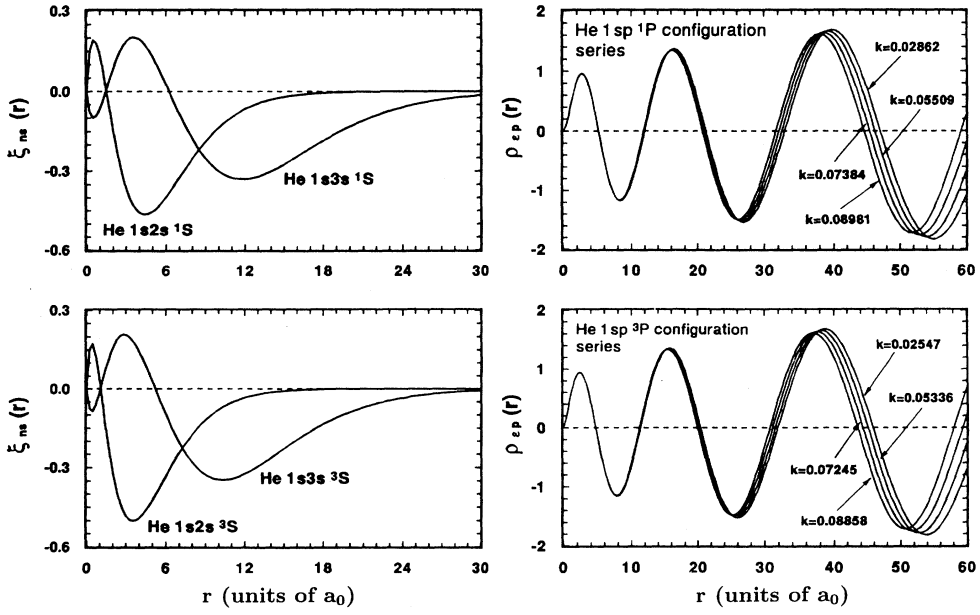

FIG. 1. Radial functions ξ_{ns} corresponding to the $1s2s\ ^{1,3}S$ and $1s3s\ ^{1,3}S$ initial states and the radial functions $\rho_{\epsilon p}$, which represent the oscillating part of the outgoing electron in the $1s\epsilon p\ ^{1,3}P$ continua. To separate ξ_{3s} from ξ_{2s}, ξ_{3s} is plotted with negative initial slope.

TABLE I. Threshold wavelengths $\lambda_{\text{threshold}}$ (in angstroms) and the $^{1,3}S \rightarrow {}^{1,3}P$ photoionization cross sections σ (in megabars) near the ionization threshold of bound excited He $1sns\ ^{1,3}S$ states with $n=2-5$. The cross sections are derived from a linear fit in λ using calculated values. The overall agreement between the length and velocity results is better than 1%. Only length results are listed.

k	$1s2s\ ^1S$	$1s3s\ ^1S$	$1s4s\ ^1S$	$1s5s\ ^1S$	$1s2s\ ^3S$	$1s3s\ ^3S$	$1s4s\ ^3S$	$1s5s\ ^3S$
				$\lambda_{\text{threshold}}$ (Å)				
0.00	3121.8	7437.3	13 567.8	21 518.6	2600.6	6634.2	12 480.7	21 305.7
				$\sigma_{1,3_{S\rightarrow}{}^{1,3}P}$ (Mb)				
0.00	9.473	14.90	21.01	27.73	5.412	7.887	10.55	13.36
0.01	9.469	14.88	20.96	27.62	5.411	7.881	10.54	13.32
0.02	9.455	14.83	20.80	27.30	5.407	7.861	10.48	13.20
0.03	9.432	14.73	20.56	26.78	5.399	7.829	10.39	13.00
0.04	9.401	14.60	20.21	26.06	5.389	7.785	10.27	12.73
0.05	9.360	14.44	19.78	25.15	5.380	7.729	10.11	12.39
0.06	9.311	14.24	19.26	24.10	5.364	7.661	9.92	12.00
0.07	9.254	14.01	18.68	22.94	5.346	7.582	9.71	11.56
0.08	9.188	13.75	18.04	21.71	5.325	7.492	9.47	11.09
0.09	9.114	13.47	17.35	20.42	5.301	7.391	9.21	10.58

for the near-threshold photoionization cross section. However, a detailed examination shows that within the dipole acceleration approximation, an additional one-particle radial matrix $\langle \rho_{\epsilon p} | 1/r^2 | \chi_{1s} \rangle$ also contributes significantly to D_{EI}. In fact, the combined contributions from $\langle \rho_{\epsilon p} | 1/r^2 | \xi_{ns} \rangle$ and $\langle \rho_{\epsilon p} | 1/r^2 | \chi_{1s} \rangle$ indeed yield a λ^{-1} dependence for the dipole matrix D_{EI}. This again leads to a linear λ dependence for the near-threshold cross section. We should note, however, that this linear λ dependence does not apply to a system such as a negative ion since the oscillating function $\rho_{\epsilon p}$ is energy dependent at small r due to the lack of long-range Coulomb interac-

TABLE II. Threshold wavelengths $\lambda_{\text{threshold}}$ (in angstroms) and the $^{1,3}P \rightarrow {}^{1,3}S$ and $^{1,3}P \rightarrow {}^{1,3}D$ photoionization cross sections σ (in megabars) near the ionization threshold of bound excited He $1snp\ ^{1,3}P$ states with $n=2-5$. The cross sections are derived from a linear fit in λ using calculated values. The overall agreement between the length and velocity results is better than 1%. Only length results are listed.

k	$1s2\ ^1P$	$1s3p\ ^1P$	$1s4p\ ^1P$	$1s5p\ ^1P$	$1s2p\ ^3P$	$1s3p\ ^3P$	$2s4p\ ^3P$	$1s5p\ ^3P$
				$\lambda_{\text{threshold}}$ (Å)				
0.00	3679.6	8263.4	14 666.9	22 892.4	3422.1	7845.9	14 097.6	22 173.7
				$\sigma_{1,3_{P\rightarrow}{}^{1,3}S}$ (Mb)				
0.00	0.947	2.764	5.366	8.650	1.020	3.004	5.796	9.293
0.01	0.946	2.759	5.347	8.605	1.019	2.998	5.776	9.245
0.02	0.944	2.742	5.292	8.470	1.017	2.981	5.718	9.103
0.03	0.939	2.714	5.200	8.251	1.012	2.952	5.621	8.872
0.04	0.933	2.676	5.074	7.952	1.006	2.911	5.489	8.556
0.05	0.925	2.626	4.909	7.554	0.998	2.858	5.313	8.132
0.06	0.916	2.567	4.719	7.113	0.988	2.797	5.114	7.670
0.07	0.905	2.500	4.507	6.636	0.977	2.726	4.892	7.171
0.08	0.893	2.425	4.278	6.141	0.964	2.648	4.652	6.650
0.09	0.879	2.344	4.039	5.639	0.950	2.563	4.400	6.122
				$\sigma_{1,3_{P\rightarrow}{}^{1,3}D}$ (Mb)				
0.00	12.50	24.13	36.21	48.97	14.95	25.54	35.84	46.43
0.01	12.48	24.08	36.08	48.73	14.94	25.49	35.73	46.22
0.02	12.43	23.92	35.71	48.00	14.89	25.35	35.41	45.60
0.03	12.36	23.66	35.10	46.81	14.81	25.11	34.88	44.58
0.04	12.25	23.31	34.27	45.19	14.71	24.79	34.14	43.20
0.05	12.10	22.84	33.17	43.07	14.57	24.37	33.19	41.39
0.06	11.94	22.29	31.91	40.68	14.40	23.87	32.09	39.35
0.07	11.74	21.66	30.49	38.10	14.21	23.30	30.85	37.12
0.08	11.53	20.97	28.97	35.39	13.99	22.66	29.49	34.76
0.09	11.28	20.21	27.36	32.63	13.74	21.96	28.06	32.34

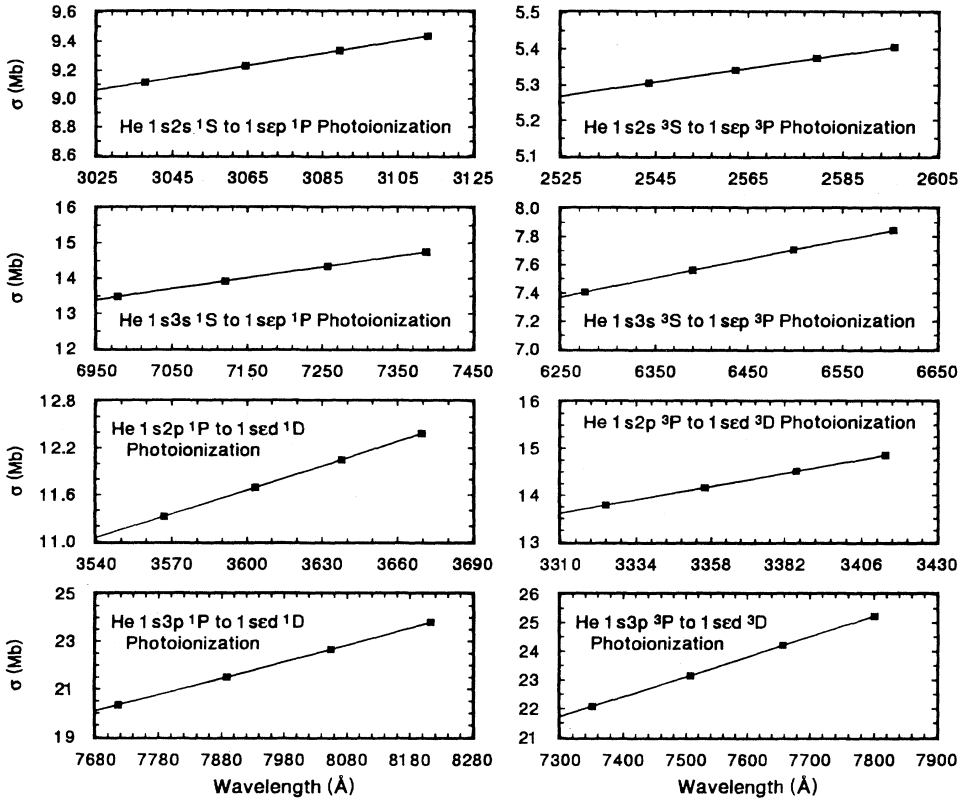

FIG. 2. Absolute cross sections for a few selected ${}^{1,3}S \rightarrow {}^{1,3}P$ and ${}^{1,3}P \rightarrow {}^{1,3}D$ photoionizations. The solid lines are fitted to the calculated values labeled by the solid squares.

tion. For many other heavier atoms (e.g., Li, Na, Mg, Ca, Zn, Rb, and Sr), the existing experimental near-threshold photoabsorption data [5] also appear to follow the linear λ dependence suggested in this paper.

III. RESULTS AND DISCUSSIONS

In Table I, the theoretical ${}^{1,3}S \rightarrow {}^{1,3}P$ cross sections σ near the He $1sns\ {}^{1,3}S$ ionization thresholds for $n=2-5$ states are tabulated. The wavelengths $\lambda_{\text{threshold}}$ and the cross sections $\sigma_{\text{threshold}}$ at the threshold (i.e., at $k=0$) are also given. In Table II, selected data for the $1snp\ {}^{1,3}P \rightarrow 1s\epsilon s\ {}^{1,3}S$ and the $1snp\ {}^{1,3}P \rightarrow 1s\epsilon d\ {}^{1,3}D$ photoionization are listed. The linear λ dependence can be seen clearly in Fig. 2 for a few selected ${}^{1,3}S \rightarrow {}^{1,3}P$ and ${}^{1,3}P \rightarrow {}^{1,3}D$ transitions. At higher energies, our calculated cross sections are in good agreement with the earlier theoretical results by Jacobs [6].

The present theory should also apply to the hydrogenlike atoms. Theoretically, according to the Kramers formula [7], the nonrelativistic cross section for the photoionization from an excited state of principal quantum number $n \geq 2$ is proportional to $(1/n^5)(\omega_G/\omega)^3$, i.e., [7]

$$\sigma_n \sim \frac{1}{Z^2}\left[\frac{\omega_G}{\omega}\right]^3 \frac{1}{n^5} = \frac{(\hbar\omega_G)^3}{Z^8}\left[\frac{\omega_n}{\omega}\right]^3 n \ , \tag{9}$$

where $\hbar\omega_G = Z^2$ Ry is the ionization energy of the hydrogenlike atom in its ground state, Z is the nuclear charge, $\hbar\omega_n = Z^2/n^2$ Ry is the ionization energy of the excited state, and $\hbar\omega = hc/\lambda$ is the energy of the incident photon. Near the threshold, $\omega = \omega_n + \Delta\omega$ and $\Delta\omega \ll \omega_n$. The energy-dependent part in Eq. (9) can be expressed approximately by

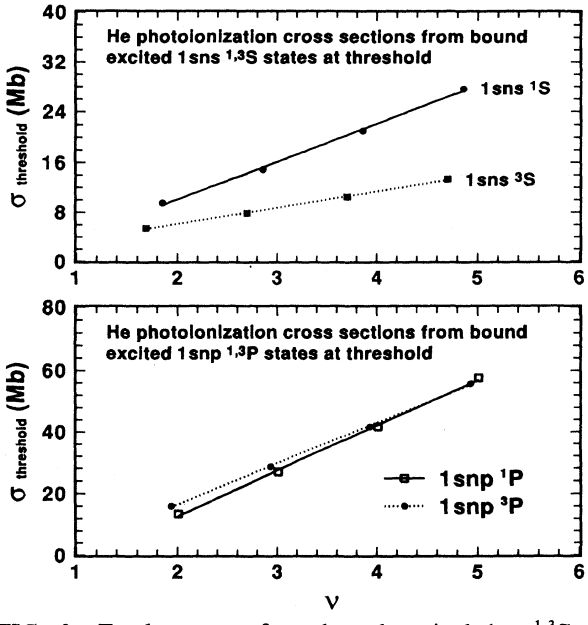

FIG. 3. Total $\sigma_{\text{threshold}}$ from bound excited $1sns\ {}^{1,3}S$ and $1snp\ {}^{1,3}P$ states as a function of the effective principal quantum numbers ν.

$$\left[\frac{\omega_n}{\omega}\right]^{\mu}=\left[1-\frac{\Delta\omega}{\omega}\right]^{\mu}\approx 1-\mu\frac{\Delta\omega}{\omega}$$
$$=(1-\mu)+\frac{\mu\omega_n}{2\pi c}\lambda\ . \qquad (10)$$

Substituting Eq. (10) into Eq. (9) leads immediately to the linear λ dependence for the near-threshold nonresonant photoionization cross section, i.e.,

$$\sigma_n\sim C_1\lambda-C_2\ , \qquad (11)$$

where C_1 and C_2 are two positive energy-independent constants. As expected, the photoionization cross section decreases as the photon energy increases (or as λ decreases). In Fig. 3, the total $\sigma_{\text{threshold}}$ from bound excited $1sns\ ^{1,3}S$ and $1snp\ ^{1,3}P$ states are plotted against ν. Similar to the nonresonant photoionization of the hydrogen atom described by Eq. (9), the total $\sigma_{\text{threshold}}$ increases *linearly* as a function of ν.

The earlier experimental near-threshold cross sections for photoionization from the He $1s2s\ ^{1,3}S$ metastable states [2] appear to support the linear λ dependence suggested in this paper. A reexamination of the experimental ratio R between the ^1S and ^3S cross sections near the $1s2s\ ^3S$ threshold is necessary to establish the quantitative accuracy of the theoretical calculation. Finally, we note that a reliable theoretical estimate of the absolute cross sections at a few selected energies from bound excited states, for transitions that are not dominated by the strong correlation effect, could potentially be used to determine experimentally the relative population densities of atoms in various excited states.

ACKNOWLEDGMENTS

This work was supported by the NSF under Grants Nos. PHY91-11420 and PHY94-13338.

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