S autoionizing states of He

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A total of 18 ^1S and ^3S autoionizing states of He below the $n = 2$, 3, and 4 ionization thresholds are calculated using the time stability theory of autoionization.

A theory of electron-atom collision resonances based on time stability was recently developed by one of us.[1] In that paper (hereafter referred to as TST) the energies and wave functions of 7 ^1S autoionizing states of He were reported. In this paper we extend the calculations to a total of 18 ^1S and ^3S autoionizing states of He.

Here TST calculations are extended to a total of 18 states. The same basis set[2] was used as in TST and calculations were again carried to four significant figures in energy. The results are reported in Table I and compared with experiment

TABLE I. ^1S and ^3S autoionizing states of He below the $n=2$, 3, and 4 ionization thresholds.[a]

n	State	Experiment	Present theory	SCC[b]	MCEB[c]	SSF[d]	MCI[e]
2	$^1S(1)$	57.82(4)[f] 57.82(5)[g] 57.83(2)[h]	57.85	57.85	57.88	57.84	57.96
	$^1S(2)$	62.06(3)[f] 62.15(5)[g]	62.10	62.14	62.14	62.09	61.16
	$^1S(3)$	62.94(3)[f] 62.95(5)[g]	62.94	62.98	63.00	62.96	···
	$^1S(4)$	64.18(3)[f] 64.22(5)[g]	64.14	(64.18)	64.20	64.10	···
	$^1S(5)$	64.67(4)[f] 64.71(5)[g]	64.33	(64.22)	64.51	···	···
3	$^1S(1)$	···	69.37	69.37	69.46	69.37	69.43
	$^1S(2)$	···	70.38	70.37	70.55	70.41	70.52
	$^1S(3)$	···	71.48	71.37	71.45	71.36	···
	$^1S(4)$	···	72.01	71.57	72.01	71.86	···
4	$^1S(1)$	···	73.54	···	73.65	73.20	73.58
	$^1S(2)$	···	73.98	···	74.07	73.92	73.96
	$^1S(3)$	···	74.48	···	74.65	74.51	74.64
	$^1S(4)$	···	75.18	···	75.37	74.55	···
2	$^3S(1)$	···	62.62	62.62	···	62.62	···
	$^3S(2)$	···	63.78	(63.82)	···	63.78	···
3	$^3S(1)$	···	71.20	···	···	71.20	···
	$^3S(2)$	···	71.66	···	···	71.66	···
4	$^3S(1)$	···	74.43	···	···	74.41	···

[a] Energies in eV above the ground state, He ground-state energy of −2.903724 a.u. was used. $\mathcal{R}_\infty = 13.605826$ eV was used to convert a.u. to eV.

[b] Scattering close-coupling calculations. $n=2$ ^1S and ^3S from P. G. Burke and A. J. Taylor, Proc. Phys. Soc. Lond. 88, 549 (1966); values in parentheses from P. G. Burke and D. D. McVicar, *ibid.* 86, 989 (1965); rest from S. Ormonde, W. Whitaker, and L. Lipsky, Phys. Rev. Lett. 19, 1161 (1967).

[c] Multiconfiguration energy bound procedure results, from E. Holøien and J. Midtdal, J. Phys. B 3, 592 (1970); 4, 32 (1971).

[d] Stationary-state Feshbach. $n=2$ ^1S and ^3S from Ref. 3; rest from R. S. Oberoi, J. Phys. B 5, 1120 (1972).

[e] Multiconfiguration interaction using Fano's (Ref. 8) theory. From D. E. Ramaker and D. M. Schrader, J. Chem. Phys. 55, 471 (1971).

[f] From Ref. 4.

[g] From M. E. Rudd, Phys. Rev. Lett. 13, 503 (1964); 15, 580 (1965).

[h] From H. Suzuki, A. Konishi, M. Yamamoto, and K. Wakiya, J. Phys. Soc. Jpn. 28, 534 (1970).

TABLE II. σ values of ^1S and ^3S autoionizing states of He below the $n=2$, 3, and 4 thresholds (in a.u.; the format A $(-n)$ represents $A\times10^{-n}$).

^1S			^3S		
$n=2$	$n=3$	$n=4$	$n=2$	$n=3$	$n=4$
7.553 (−4)	1.880 (−4)	1.319 (−4)	2.300 (−6)	4.763 (−6)	9.349 (−5)
3.975 (−5)	2.244 (−4)	1.601 (−4)	4.827 (−6)	1.216 (−5)	•••
3.495 (−4)	4.337 (−4)	2.241 (−4)	•••	•••	•••
8.597 (−5)	2.971 (−5)	3.020 (−4)	•••	•••	•••
1.113 (−3)	•••	•••	•••	•••	•••

and calculations based on other methods. The comparison is by no means exhaustive. Only representative results of various methods are included. The time-stability spectrum was used to find the states of higher thresholds. $\mathcal{R}_\infty = 13.605\,826$ eV was used to convert a.u. to eV (Bhatia and Temkin[3] show that this is a better procedure if one wants to compare calculations with electron-atom collision experiments).

Our result for the second ^1S autoionizing state supports the calculations of Bhatia and Temkin[3] and the Hicks and Comer's experimental value[4] rather than other theoretical and experimental values which slightly disagree with the former. Our results should be more dependable when the principal quantum numbers of the two electrons are not too far apart since the Kinoshita basis was primarily designed to represent two electrons in the same region of space. The discrepancy between our fifth ^1S calculation and experiment might be due to this reason since this state probably has a $2s4s$ configuration. The σ values we found are reported in Table II. All calculations were done on an IBM 370/145.

We would like to take this opportunity to call attention to three references which were inadvertently overlooked in TST.

Read[5] used the minimization of σ to calculate autoionizing states of He. He even used graphs similar to TST's time-stability spectrum, although he plotted σ versus λ [cf. Eq. (3)] rather than $\tau = 1/\sqrt{\sigma}$ versus $\langle H\rangle$. He minimized $\langle(H-E)^2\rangle$ for various E, but in effect ended up using the iteration suggested in TST.

Smith[6] treated resonances as maxima in the time delay of a projectile particle in scattering, a concept parallel to TST. The peaks of his time-delay matrix should correspond to the peaks of our time-stability spectrum.

Froelich and Brändas[7] arrived at practically the same method (i.e., the minimization of σ) using different considerations. They applied the theory to resonances in the Stark effect in H with success. They also showed that this method does not involve a Δ shift and that the results can be compared with experiment without any additional corrections.

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