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Electron affinity of helium $(1s2s)^3S$

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A configuration-interaction calculation with a carefully optimized orbital basis gives an upper bound $E_u = -2.178040$ a.u. (He) for the nonrelativistic energy E_{nr} of the $(1s2s2p)^4P^0$ metastable state of the He negative ion. Extensive studies of patterns of convergence for the energy show that $E_{nr} = -2.178074(10)$, which together with Pekeris' accurate E_{nr} He $(1s2s)^3S$ yields a nonrelativistic electron affinity $A_{nr} = 77.4(3)$ meV. It is argued that the true electron affinity should not differ from A_{nr} by more than ± 0.2 meV. Good agreement with the less-precise experimental values is obtained. The present results, by allowing a recalibration of the experiments, will permit a significant increase in the accuracy of future experimental determinations of electron affinities below 300 meV.

I. INTRODUCTION

Atomic electron affinities (A's) can now be experimentally determined with unprecedented accuracy (±0.3 meV) by means of tunable laser photodetachment spectroscopy (LPS)[1] in the energy range 1.5–5.0 eV of the laser photons. Photodetachment into excited states[2] rather than into the ground state of the neutral atom, has allowed LPS determinations of the A's of the alkali-metal atoms, which are in the 0.5 eV energy range. Laser photodetached electron spectroscopy (LPES),[3] first used by Hall and co-workers[4] in the determination of the electron affinity of He $(1s2s)\,^3S$, on the other hand, is not limited to studying systems with a minimum binding energy. Its present accuracy[1] (±3 meV), however, compares unfavorably with LPS. These and other pertinent experimental techniques have been recently reviewed.[1]

On the theoretical side, accurate calculations of A's are severely limited by the size of the atomic system. Except for the stable H^- ion, whose A is considered to be known theoretically with an uncertainty of ±0.003 meV,[1] and for the Li^- ion for which the relative ease of the calculations allows A to be predicted with an uncertainty of 7 meV,[5] extensive and conscientious[6] calculations for larger systems end up with uncertainties of 100–300 meV. As illustrated in a recent publication,[7] the theoretical determination of A's to within 10 meV appears at present as a difficult challenge.

The $(1s2s2p)\,^4P^o$ metastable state of the He negative ion offers an example where a good approximation to a full configuration interaction (CI) treatment is feasible, the only difficult task being the development of a compact orbital basis.[8] The A may be written

$$A = A_{nr} + A_{\text{rel}} + A_{\text{rad}} + A_{mp}, \tag{1}$$

where the subscripts stand for nonrelativistic, relativistic, radiative, and mass polarization. In He^-, the fine and hyperfine structure splittings[9,10] are less than 2 μhartree, and therefore they may be neglected. In Table I we present the energy corrections $\Delta E = E_{\text{exp}} - E_{nr}$ for several He states at various stages of ionization. The increase in ΔE when adding a $2s$ or a $2p$ electron to He^+ $1s$ is about 7 or 8 μhartree. In the present calculation, we have verified that the addition of an extra electron to form the $(1s2s2p)\,^4P^o$ negative ion causes a relatively small reaccomodation of the $2s$ charge distribution, leaving the inner $1s$ core almost intact. Therefore, it is to be expected that the increase in ΔE due to the formation of the negative ion should not be larger in magnitude than the increase in ΔE when forming the neutral excited states from He^+ $1s$. We have then assigned $\Delta E = -0.000\,098(8)$ a.u. for the $(1s2s2p)\,^4P^o$ state of He^-, which is equivalent to writing

$$A = A_{nr} \pm 8\,\mu\text{hartree}\ (\pm 0.2\ \text{meV}). \tag{2}$$

It is then desirable to calculate A_{nr} with comparable accuracy. This is achieved by means of a CI calculation which we describe in Sec. II.

Our calculated $A = 77.4(5)$ meV can then be used to calibrate less-precise LPES and other experiments, as discussed in Sec. III.

Previous theoretical work includes (i) a 28-term CI calculation by Weiss,[11] giving an $A = 69$ meV, (ii) a calculation[12] of the lifetime of the $^4P_{5/2}$ state $\tau = 4.55 \times 10^{-4}$ sec, which is in good agreement with experimental results,[13] and (iii) a study[9] of the fine and hyperfine-structure constants and lifetimes of the fine-structure levels.

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TABLE I. Correction $\Delta E = E_{\text{exp}} - E_{nr}$ for several He states at various ionization stages, in a.u. (He).

State	E_{nr}	ΔE
$1s$ He$^+$	-2.0	$-0.000\,090\,1$ [a]
$(1s2s)\,^3S$ He	$-2.175\,229\,3$	$-0.000\,097\,8$ [b]
$(1s2p)\,^3P$ He	$-2.133\,164\,1$	$-0.000\,097\,5$ [b]
$(1s2s2p)\,^4P^o$ He$^-$	$-2.178\,074$ [c]	$-0.000\,098\,(8)$ [d]

[a] J. D. Garcia and J. E. Mack, J. Opt. Soc. Am. 55, 654 (1965).

[b] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A 4, 516 (1971).

[c] See Table III.

[d] See text.

Another aspect linked to a sequence of increasingly accurate wave functions is the possibility to test the theory of the relativistic and radiative corrections.[10] Work in this direction is in progress at our laboratory.

II. CALCULATIONS AND RESULTS

Our implementation of CI techniques to carry out atomic calculations based on (i) a Slater-type orbital (STO) basis, (ii) orthogonal symmetry adapted orbitals, and (iii) L-S eigenfunctions, has been described previously.[14,15]

A. STO basis

The present calculation has been particularly difficult on account of the delocalization of the STO basis. The range covered by the STO's extends from 0.75 to 17 bohr, and the STO distribution along the radial coordinate is sparse and unexpected. Since the precision we wish to attain is of the order of ± 0.2 meV $= 8$ μhartree, it is important to carry out exhaustive analyses of the convergence of the energy with respect to truncations of the STO basis (truncations to the full Cl expansion are found to be negligible). To that end we were forced[16] to develop a small, critical STO basis which would remain invariant after inclusion of additional STO's and further reoptimizations.

In Table II we give the $8s9p5d4f1g$ STO basis together with the complementary STO's utilized in studies of patterns of convergence for the energy. A straightforward analysis[15] of the convergence of the pair energies was impaired by the wide degree of delocalization of the STO's. Instead, we examined, for each harmonic, the convergence of the energy as we attempted to saturate a given re-

TABLE II. STO parameters. The functions marked with an asterisk form the critical $4s4p2d$ STO basis. Sequential optimization of additional STO's is sufficient to provide a fully optimized $8s9p5d4f1g$ basis, i.e., one which is stable upon cyclic reoptimization of any one of its members. The truncation energy errors require several CI calculations which include all single and double excitations, and a STO basis extended with the STO's enclosed between parentheses.

l	STO's	Truncation energy errors, in μhartree
0	$1s^*=2.0$; $2s^*=0.72$; $2s^*=0.345$; $3s^*=0.835$; $4s=1.05$; $3s=0.40$; $3s=3.30$; $5s=2.1$ ($4s=6.0$; $4s=4.5$; $4s=3.6$; $4s=3.0$) [a] ($5s=1.9$; $6s=2.03$; $5s=1.43$; $6s=1.35$) [b] ($4s=0.67$; $4s=0.58$; $5s=0.67$; $5s=0.58$) [c]	8 ± 2
1	$2p^*=0.53$; $2p^*=0.30$; $2p^*=0.15$; $3p^*=0.76$; $4p=0.97$; $4p=0.39$; $2p=2.0$; $3p=1.65$; $5p=1.9$ ($4p=3.6$; $4p=2.65$; $4p=1.8$) [a] ($5p=1.4$; $5p=1.05$; $5p=0.9$) [b] ($3p=0.35$; $3p=0.27$; $3p=0.18$) [c]	9 ± 3
2	$3d^*=0.38$; $3d^*=0.80$; $4d=0.47$; $3d=1.80$; $4d=1.80$ ($5d=4.2$; $5d=3.4$; $5d=2.5$; $5d=1.8$) [a] ($4d=1.2$; $4d=1.0$; $4d=0.85$; $4d=0.7$) [b] ($5d=0.63$; $5d=0.55$; $6d=0.55$; $7d=0.55$) [c]	11 ± 3
≥ 3	$4f=0.70$; $5f=0.75$; $4f=2.5$; $5f=2.5$; $5g=0.85$ ($6f=2.5$; $7f=2.5$; $5f=4.6$; $6f=4.3$; $6g=3.1$; $7g=3.1$) [a] ($6f=0.75$; $7f=0.75$; $6f=1.0$; $6g=0.9$; $7g=0.95$) [c]	6 ± 2
	Total	34 ± 10

[a] STO's localized in the intershell $1s$-$2s$ region to account for truncation energy errors.

[b] Same as a but localization is in the $2s$ and $2s$-$2p$ region.

[c] Same as a but localization is further out from the $2p$ region.

gion with as many STO's as we could handle. For example, in order to estimate STO truncation errors for $l=0$, Δ_0, we performed three CI calculations including all single and double excitations and $12s9p5d$ STO's with the complementary STO's localized in different regions, as explained and shown in Table II. The three CI results were then analyzed in terms of $\epsilon(2s)$, $\epsilon(2s2p)$, $\epsilon(1s2p)$, and $\epsilon(1s2s)$ excitation energies. The lower limit for Δ_0, $\Delta_0^< = 6$ μhartree is the largest energy difference between the $8s9p5d$ and the $12s9p5d$ CI's. The upper limit to Δ_0, $\Delta_0^> = 10$ μhartree, was computed by judiciously adding the increments in excitation energies, neglecting some contributions which seemed to be duplicated on account of similarities between CI coefficients and closeness of STO's. In this way we get $\Delta_0 = 8 \pm 2$ μhartree, as reported in the last column of Table II. The straightforward addition of the three CI energy differences gives a $\Delta_0^> = 14$ μhartree, or $\Delta_0 = 10 \pm 4$ μhartree, which we feel to be unrealistic. We finally obtain an empirical STO truncation error of 34 ± 10 μhartree (see Table II).

B. Nature of binding in He⁻

CI calculations with extended STO bases show that the $(1s2s2p)\,^4P^o$ state of He^- is not bound unless one includes d-type STO's. Thus the sp-energy limit is not bound: as one optimizes the energy, the STO's reaccomodate themselves to represent the $(1s2s)\,^3S$ state of He plus a free electron. As a consequence, the lowest-energy self-consistent-field (SCF) solution does not correspond to an absolute minimum, and in matrix Hartree-Fock calculations the range of the p-type STO parameters must be constrained to avoid the running away of the $2p$ orbital.

In Table III we show the first twelve configurations of the $(1s2s2p)\,^4P^o$ wave function expressed in terms of approximate natural orbitals. The energy contributions of each configuration are also given. The energy of the first configuration coincides with that found by Holøien[17] a long time ago. Binding of the outer electron takes place after including the third configuration. The first four configurations account for more than one half of the binding energy, but thereafter the A converges at a slower rate. The $A = 72.9$ meV given by the first 30 terms is very close to the 69 meV obtained by Weiss[11] with a 28-term CI expansion. The last 0.9 meV to the A are provided by the STO's not included in the final wave function (see previous and following subsections).

C. Electronic energy of the $(1s2s2p)\,^4P^o$ state

In Table IV we summarize the results of the calculation of the electronic energy of He^-. A 300-term CI expansion gives a rigorous upper bound to the nonrelativistic energy $E_u = -2.178\,040$ a.u. (He). The truncation energy error ΔE_{tr} due to trunca-

TABLE III. First twelve configurations of the He^- wave function expressed in terms of approximate natural orbitals. Binding of the outer electron is obtained after including the third configuration. The convergence of the A slows down after the first 30 configurations. The electron detachment threshold is at $E(1s2s\,^3S) = -2.175\,23$ a.u. (He).

Configuration	Excitation	CI coefficient	Approximate energy [a] contribution in a.u. (He)	A, [b] in meV
$s_1s_2p_1$		0.977	−2.170 07	−123.2
$s_1p_1d_1$	$s_2 \rightarrow d_1$	−0.144	−0.002 57	− 53.3
$s_1s_3p_2$	$s_2p_1 \rightarrow s_3p_2$	0.129	−0.002 37	11.2
$s_1p_2d_1$	$\rightarrow p_2d_1$	−0.087	−0.001 13	41.9
$s_1p_3d_1$	$\rightarrow p_3d_1$	0.012	−0.000 06	43.5
$p_1(p_2p_3)\,^3S$	$s_1s_2 \rightarrow p_2p_3$	0.010	−0.000 23	49.8
$p_1(p_3p_4)\,^3S$	$\rightarrow p_3p_4$	−0.007	−0.000 18	54.7
$s_1p_4d_1$	$s_2p_1 \rightarrow p_4d_1$	0.007	−0.000 06	56.3
$s_2p_3d_2$	$s_1p_1 \rightarrow p_3d_2$	0.007	−0.000 13	59.8
$s_1d_1f_1$	$s_2p_1 \rightarrow d_1f_1$	−0.007	−0.000 05	61.2
$p_1^2p_3$	$s_1s_2 \rightarrow p_1p_3$	−0.007	−0.000 11	64.2
$s_2s_3p_3$	$s_1p_1 \rightarrow s_3p_3$	0.006	−0.000 05	65.6
30-term CI				72.9
200-term CI				76.4
300-term CI				76.5 [c]
745-term CI				76.5
A_{nr}				77.4(3) [c]

[a] Approximate energy contributions of each configuration.
[b] Contributions to the A of all configurations up to a given order.
[c] Data derived from Table IV.

TABLE IV. Electronic energy for the $(1s2s2p)\,^4P^o$ state of He^-, in a.u. (He) and electron affinity of He $(1s2s)\,^3S$. 1 a.u. (^{4}He) = 219 444.53 cm^{-1} = 27.207 91(10) eV.

	Energy correction	Total energy
E_u, 300-term CI		−2.178 040
Truncation error, full CI	negligible	
Truncation error, STO basis	−0.000 034(10) [a]	
$E_{nr}=E_{\mathrm{CI}}$ [a]		−2.178 074(10)
A_{nr}	−0.002 845(10) [c] = 77.4 ± 0.3 meV	
$\Delta E = E_{\mathrm{exp}} - E_{nr}$	−0.000 098(8) [d]	
E_{exp}, predicted		−2.178 172(18)
A Eq. (2)	−0.002 845(18) = 77.4 ± 0.5 meV	

[a] Taken from Table II.

[b] E_{CI} is the limiting CI energy value, taken to be equal to the exact eigenvalue E_{nr} of the nonrelativistic Schrödinger's equation, see text.

[c] Using $E(1s2s\,^3S) = -2.175\,229$ a.u. (He), taken from Table I.

[d] Taken from Table I.

tions in the full Cl expansion is very small, $\Delta E_{tr} < 1$ μhartree = 0.03 meV. If we add to E_u the 34 ± 10 μhartree energy error introduced by the truncation of the STO set (see Table II), we arrive at the limiting value $E_{\mathrm{Cl}} = -2.178\,074(10)$ for the CI energy in a complete basis. We have assumed that E_{Cl} is equal to the exact eigenvalue E_{nr} of the nonrelativistic Schrödinger's equation. Thus we have neglected any *possible* significant energy contribution from terms which appear in the many-electron coalescence regions.[18]

Our final result for the electron affinity of He $(1s2s)\,^3S$ is

$$A = 77.4 \pm 0.5 \text{ meV}, \tag{3}$$

as shown in the last row of Table IV.

D. Comparison of calculated and experimental A's

In Table V we compare our calculated A with experimental values. It may be seen that there is good agreement with the less precise experimental values. This theme is pursued in Sec. III.

TABLE V. Comparison of calculated and experimental electron affinities for He $(1s2s)\,^3S$, in meV.

Method	Electron affinity
LPES	79 ± 2 [a]
Field ionization	75 ± 5 [b]
Calculation, this work	77.4 ± 0.5 [c]

[a] Ref. 4; ±2 meV is the probable error. The limit of error (95% confidence) is ±8 meV. The A given in Ref. 4 is 1 meV higher because the A of the reference ion H^- was taken as 755.1 meV instead of 754.2.

[b] Ref. 20; treatment of filed spectra yields 75.2(5) meV, but systematic errors amount to ±5 meV. Y. N. Demkov and G. F. Drukarev, Zh. Eksp. Teor. Fiz. 47, 918 (1964) [Sov. Phys.-JETP 20, 614 (1965)], using the field ionization results of Ref. 19, gave evidence leading to an $A = 85 \pm 15$ meV.

[c] Taken from Table IV.

III. DISCUSSION

In Sec. II we obtained $A = 77.4(5)$ meV for the binding energy of He^- relative to He$(1s2s)\,^3S$. This result has immediate practical consequences. We now discuss how to improve the application of two experimental methods to determine A's of weakly-bound systems.

A. LPES

This technique is well documented in the literature.[3] The A_2 of system 2 is determined relative to the A_1 of system 1 which is well known either from theory (H^-, D^-) or from the more precise LPS experiments.[1] The crucial quantity to be measured is the difference between the kinetic energies of the photodetached electrons, Ω_1-Ω_2, which enters the equation for the electron affinity as[3]:

$$A_2 = A_1 + (\Omega_1 - \Omega_2) + mW(1/M_1 - 1/M_2)\ , \tag{4}$$

where M_1 and M_2 refer to the masses of systems 1 and 2, m is the electron mass, and W is the kinetic energy of the negative ion. The third term on the right-hand side of Eq. (4) is important when H^- or D^- are used as reference ions. For a beam energy of 700.00 ± 0.25 eV, such as used in this kind of experiments,[3,4] the kinematic correction is of the order of 380 meV/amu, for $M_2 > M_1$, with a relatively small uncertainty of ±0.1 meV due to the beam-energy spread of ±0.25 eV.

The energy difference Ω_1-Ω_2 has a typical standard deviation of 0.4 meV,[3] but systematic errors, due to nonlinearities in the energy scale of the electron energy analyzers, produce an additional 0.5% of error. Therefore, in order to get a precise value for A_2, it is desirable to have a small $\Omega_1-\Omega_2$ value, i.e., a reference ion with A_1 close to A_2. The K$^-$ ion, with an $A = 501.2(5)$ meV,[2] should be the best reference ion for $300 < A_2 < 700$ meV, assuming a beam energy of 700 eV and the experimental errors quoted in Ref. 3. When $A_2 \simeq 300$ meV, the uncertainty in $\Omega_1-\Omega_2$ is ± 1.0 meV for K$^-$ as a reference ion, while it is only ± 0.6 meV for He$^-$ as a reference ion. Clearly, for $A_2 < 300$ meV, He$^-$ is superior to K$^-$ as a reference ion, the optimum range being around $A_2 \simeq 172$ meV for a beam energy of 700 eV.

B. Field ionization

The possibility of electron detachment from He$^-$ under the influence of an electric field was first demonstrated by Riviere and Sweetman.[19] By measuring the attenuation of a beam of negative ions as it goes through an external electric field, Oparin *et al.*[20] have determined A's in a number of negative ions with binding energies <100 meV. Aside from the approximations involved in the theory[21] which underlies the interpretation of the experimental data, the main error appears to be in the determination of the field intensity, which amounts to 10% and propagates an error of 7% in the A. If the accuracy of the theory[21] as applied to He$^-$ may be trusted,[22] our computed A for He$^-$, which is accurate to 0.7%, may be utilized to calibrate the electric field intensity to within 1%. Several additional reference ions with A's <100 meV may be necessary to further refine the application of this experimental method.

C. Other excited states of He$^-$

Beck and Nicolaides have recently[23] demonstrated the metastability of the $(2p^3)\,^4S^o$ state of He$^-$ by showing that it lies below the continuum with the same symmetry and parity, i.e., the $^4S^o$ state is below the $(2p^2)\,^3P$ metastable state of neutral He. For a long time,[24] the existence of a long lived even-parity ^2P state of He$^-$ has been suspected by experimentalists. We have carried out fairly extensive calculations for these ^2P states, without assuming any specially preferred configurations, and found no binding relative to the $(1s2p)\,^3P$ He threshold. We conclude that there are no long-lived ^2P states of He$^-$.

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