Triply excited bound state of He⁻ and the isoelectronic sequence

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The energy level of the $^4S^o$ state of He⁻ is found to be lower than that of the $(2p2p)\,^3P$ state of He by about 0.328 eV. It is metastable against autoionization and decays through radiation to the triply excited autoionization state of $^4P^e$ and its associated continuum. For Li and three-electron positive ions, the $^4S^o$ state also decays to the doubly excited $^4P^e$ bound state. The energy levels of these states are calculated and transition wavelengths are also predicted.

Most of the triply excited states of atomic systems lies in the continuum and couple to the continuum through Coulomb interaction between the electrons.[1] The $^2S^o$ and $^4S^o$ states of the three-electron systems are two exceptions. For the $^4S^o$, the predominate configuration is composed of a $(2p2p)\,^3P$ core together with the third $2p$ electron to form an S state. In the LS scheme,[1] it does not couple to any three-electron configuration with an s orbital because of parity violation. Hence, it is a bound state if the energy level lies below the $(2p2p)\,^3P$ threshold. For Li and three-electron positive ions, the bound states can always be formed due to the nuclear Coulomb potential. However, for negative ions, the nature of the interaction is different. It is therefore of interest to know if a bound state does exist in these systems. To my knowledge, this is the first variational calculation concerning the existence of this state for He⁻. As for $^2S^o$, the third electron would be a $3p$ orbital due to the Pauli antisymmetric principle. Hence the energy will be higher and no bound state of this symmetry is found for the helium negative ion. The calculation is done using the Rayleigh-Ritz variational method[2] with a nonrelativistic Hamiltonian of the three-electron system. The Schrödinger equation is given by

$$H\Psi = E\Psi , \tag{1a}$$

where

$$H = -\sum_{i=1}^{3}\left(\frac{1}{2}\nabla_i^2 + \frac{1}{r_i}\right) + \sum_{i<j}^{3}\frac{1}{zr_{ij}} ; \tag{1b}$$

z is the charge of the nucleus. This Hamiltonian is obtained by a transformation of $zr \rightarrow r$. Therefore the true energy would be $E_{\text{true}} = z^2 E$. The trial function is the product of the radial, angular, and spin parts which are given by, respectively,[3]

$$\phi_{mnk}(r_1, r_2, r_3) = r_1^m r_2^n r_3^k e^{-\alpha r_1 - \beta r_2 - \gamma r_3} , \tag{2a}$$

$$Y^{l_3;LM}_{l_1 l_2; l_{12}}(\hat{r}_1, \hat{r}_2, \hat{r}_3)$$

$$= \sum_{\substack{m_1 m_2 \\ m_3 \mu}} Y^{m_1}_{l_1}(\hat{r}_1)\, Y^{m_2}_{l_2}(\hat{r}_2)\, Y^{m_3}_{l_3}(\hat{r}_3) \tag{2b}$$

$$\times \langle l_1 l_2 m_1 m_2 | l_{12}\mu\rangle\langle l_{12}l_3 \mu m_3 | LM\rangle$$

and the spin part $\chi(1, 2, 3)$ is symmetric with respect to permutation. It is given by the usual quartet representation in the standard text.[4] α, β, and γ are the nonlinear parameters. Thus the total wave function is given by

$$\Psi_{LM} = A\sum C^{l_1 l_2 l_{12} l_3}_{mnk}\phi_{mnk}(r_1, r_2, r_3) Y^{l_3;LM}_{l_1 l_2; l_{12}}$$

$$\times (\hat{r}_1, \hat{r}_2, \hat{r}_3)\chi(1, 2, 3) \tag{3}$$

where A is the antisymmetrization operator. The summation is over all possible m, n, k, l_1, l_2, l_{12}, l_3. C's are the linear parameters to be optimized in the variation process.

The binding nature of the $^4S^o$ becomes evident as only one angular partial wave $[(1, 1)_1; 1]0$ is included in the computation. Here I have used a notation $[(l_1, l_2)_{l_{12}}; l_3]L$ for easier discussion. In the final calculation, a 77-term wave function is used in which three angular states $[(1, 1)_1; 1]$, $[(2, 2)_1; 1]$, $[(3, 3)_1; 1]$ with several combinations of α, β, and γ included. Table I gives the convergence pattern in this calculation. The upper bound for the energy of this state is found to be $-0.722\,546$ a.u. If compared with the helium $(2p2p)\,^3P$ bound state energy[5] of $-0.710\,498$ a.u. it is lower by about 0.328 eV. The upper bound for the Li $^4S^o$ state is found to be $-2.103\,13$ a.u. For higher nuclear charges, the energy converges faster and only a 57-term wave function is used.

The $^4S^o$ state decays to the lower $^4P^e$ state through radiation. In an earlier work,[6] it was reported that a $^4P^e$ bound state exist for He⁻. However, in this work I failed to locate this bound state with a 75-term trial function, although this function gives an electron affinity of 0.66 eV for $^4P^o$ He⁻ with only one set of α, β, and γ. This

TABLE I. Convergence of $^4S^o$ state of He⁻.[a]

N	K	E (a.u.)
22	1	−0.710 734
29	2	−0.721 708
36	3	−0.722 267
46	3	−0.722 453
77	3	−0.722 546

[a]N is the total number of linear parameters in the wave function. K is the number of angular partial waves used.

is twice that of Ref. 6, but it agrees with the result of Weiss[7] and others.[8] The present work can not rule out the possibility of the existence of a He⁻ $^4P^e$ bound state, but it seems reasonable to assume that if bounded it will lie extremely close to the He$(1s2p)$ ^3P threshold. It is believed in some literature that $^4P^o$ is the only bound state for He⁻ in the doubly excited energy region.[9]

In Fig. 1 an energy diagram for the He⁻ $^4S^o$ and related states are shown. Aside from the transition to the continuum there is one autoionizing $(2s2p2p)$ $^4P^e$ state which lies below the He$(2s2p)$ ^3P threshold by about 0.88 eV. The transition wavelength from $^4S^o$ to this autoionizing state is about 6458 Å. The calculation of this autoionizing state is more involved and will be published elsewhere.

In Table II, the energies of the lowest members of the $^4S^o$ and $^4P^e$ states and its corresponding transition wavelength are given. The radiation lifetime of these $^4S^o$ states ranges from about 10^{-10} to 10^{-12} sec. It is perhaps of interest to note that the $^4P^e$ state of O^{5+} and F^{6+} in this table further improves the agreement between the existing theoretical and experimental results.[10,11] This is also true for Li as compared with the experiments of Levitt et al.[9] Ahlenius and Larsson recently computed the $^4P^o$ state of Li using a 53-term trial function with r_{12} explicitly included; they obtained

TABLE II. $^4S^o$ and $^4P^e$ energies for Li to F^{6+} (in a.u.).

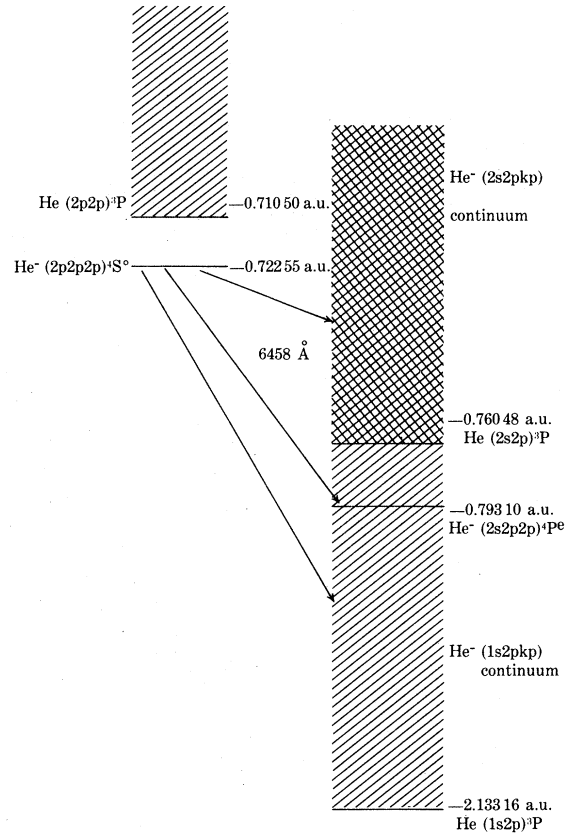|	$^4S^o$	$^4P^e$	Transition wavelength (Å)
Li	−2.103 13	−5.245 08	145.016
Be⁺	−4.235 84	−9.870 22	80.867
B^{2+}	−7.118 73	−15.999 64	51.305
C^{3+}	−10.751 62	−23.630 92	35.377
N^{4+}	−15.134 50	−32.763 22	25.846
O^{5+}	−20.267 37	−43.396 13	19.700
F^{6+}	−26.150 23	−55.529 40	15.509

FIG. 1. Energy diagram for the $^4S^o$ state of He⁻. The threshold energies are from He$(2p2p)$$^3P$, Ref. 5; He$(2s2p)$$^3P$, A. K. Bhiatia and A. Temkin, Phys. Rev. A 11, 2018 (1975); He$(1s2p)$$^3P$, C. Pekeris, Phys. Rev. 137, A1672 (1965).

−5.367 80 a.u. for the energy of this state.[12] The accurate measurement of Levitt and Feldman[13] gives 0.122 63 a.u. for the $^4P^e$-$^4P^o$ transition. This resulted in an energy of −5.245 17 a.u. lower than the present work of −5.245 08 a.u. by about 0.0024 eV. Calculations of the $^4S^o$ state have been made by Safronova and Senashenko[14] who carried the perturbation theory to second order. The energy they obtained is not an upper bound to the true energy for a bound state due to the $2n + 1$ theorem.[15] The third-order energy will be positive therefore their result could be raised substantially. This is why their energy falls below the energy calculated here for $z = 3$ to 9. They have not made any claim on the existence of the $^4S^o$ state for He⁻.

ACKNOWLEDGMENT

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