

Bound states and decay mechanisms of He^-

Cleanthes A. Nicolaides* and Yannis Komninos

Theoretical and Physical Chemistry Institute, N. H. R. F., 48 Vas. Constantinou Avenue, Athens 501, Greece

Donald R. Beck†

Physics Department, University of Illinois, Urbana, Illinois 61801

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Detailed electron-correlation calculations which include the mixing of closed channel with open channels, suggest that He^- has only two bound states: The $1s2s2p\ ^4P^o$ and the $2p^3\ ^4S^o$. The $1s2p^2\ ^4P$ and 2P states are above the $\text{He}\ 1s2p\ ^3P^o$ threshold and therefore qualify only as core-excited shape resonances. This conclusion contradicts certain previous theoretical and experimental findings which implied the existence of bound He^- 4P and 2P states. Both $^4P^o$ and $^4S^o$ autoionize to the adjacent continuum via spin-dependent forces—a well-known decay mechanism. However, there are two more decay mechanisms: nonrelativistic (for $^4S^o$) and relativistic (for $^4P^o$) radiative autoionization (RA). The probability for RA of the $^4S^o$ state in the Hartree-Fock approximation is computed to be $1.14 \times 10^{10}\ \text{sec}^{-1}$.

I. INTRODUCTION

Like every nonrelativistic negative ion, He^- has a finite number of bound states. Which ones? And how do they decay?

In 1967, Holþien and Geltman¹ predicted that He^- has at least two bound states, the $1s2s2p\ ^4P^o$ with affinity $E_A > 0.033\ \text{eV}$ and the $1s2p^2\ ^4P$ with $E_A > 0.20\ \text{eV}$. At approximately the same time, electric-field-quenching² and laser-photodetachment³ experiments yielded $E_A(^4P^o) = 0.080 \pm 0.002\ \text{eV}$.³ It was argued that both the $^4P^o$ and the 4P states decay via relativistic autoionization to the $\text{He}\ 1s^2$ continuum.^{1,4,5} The predicted as-bound $1s2p^2\ ^4P$ has never been observed. However, in 1975 Baragiola and Salvatelli⁶ and, more recently, Dunn *et al.*⁷ have obtained experimental results which, together with previous evidence, were interpreted as suggesting the existence of another bound state, the $\text{He}^- 1s2p^2\ ^2P$. Similarly, Safronova and Senashenko⁸ suggested that the 2P state is indeed bound but that the 4P is not. (For 4P and 2P to be bound they must be below the $\text{He}\ 1s2p\ ^3P^o$ state which is 20.96 eV above $\text{He}\ 1s^2\ ^1S$). This is surprising since one would expect the 4P state to lie below the 2P .

Recently, He^- was examined theoretically by Beck and Nicolaides⁹ and Bunge and Bunge.^{10,11} The Bunges reported that the $1s2s2p\ ^4P^o$ state is bound by 0.077 eV but that the 4P and 2P "states" are not. On the other hand, we found that there is yet another, much-higher-lying state of He^- which is bound: the spherically symmetric, triply excited $2p^3\ ^4S^o$.

In this note we report the results of our analysis of the He^- discrete spectrum. This analysis establishes that the only bound states of He^- are the $1s2s2p\ ^4P^o$ and $2p^3\ ^4S^o$ and that their decay mecha-

nisms involve not only radiationless but also radiative transitions to the continuum.

II. THEORY AND RESULTS

Having already determined that $\text{He}^- 2p^3\ ^4S^o$ is bound,⁹ (see also the Appendix) we recently turned our attention to the $1s2p^2\ ^4P$ and 2P states. We thought that a definitive calculation which would include the effect of the continuum, would clarify the uncertainty as to their exact position and related questions of radiative transitions. We were also interested in studying the behavior of the electron correlation of these states in view of apparent anomalies in the conclusions of previous work. For example, the 2P was predicted⁸ to lie below the 4P state—against Hund's rules. And although Hund's rules need not hold for highly excited states—due to the extreme importance of electron correlation and the occasional breakdown of the independent particle model (IPM)—for these states, simple rules of atomic structure¹² beyond the IPM predict the effects of electron correlation to be smooth.

On the other hand, when we extracted from the experimental positions of the $\text{He}\ 1s2p\ ^3P^o$ and $2p^2\ ^3P$ states correlation energies for these pairs (0.046 and 0.244 eV, respectively) and added them to the Hartree-Fock energies of the $1s2p^2\ ^4P$ and 2P configurations (−2.1204 and −2.1158 a.u., respectively) neither of these states fell below the $\text{He}\ 1s2p\ ^3P^o$ threshold. These findings, although not conclusive, are corroborated by the recently reported negative results of large-configuration-interaction (CI) calculations.^{10,11} Nevertheless, although CI calculations with square-integrable orbital basis sets may obtain good convergence, they cannot be considered definitive when applied to configurations which lie in the continuum. This

is because the mixing of the open-channel scattering functions may cause a different energy shift than the one obtained implicitly in a total CI calculation (see below). For a state very close to threshold, as for example the 4P state, such a shift may conceivably have a sufficient magnitude to "create" a bound state out of a continuum wave packet. Thus, we decided to examine the 4P and 2P states from first principles, using our variational methods for obtaining electron correlation¹³ and including the effect of the mixing of the closed with the open channels.

The exact wave function is expressed in the symbolic notation¹³

$$\psi = \phi_{\text{HF}} + \phi_{\text{HF}}^{-1} \sigma(r_1) + \phi_{\text{HF}}^{-2} \pi(r_1 r_2) + \tau(r_1 r_2 r_3), \quad (1)$$

where σ , π , and τ are symmetrized one-, two-, and three-electron subshell clusters. For both the 4P and 2P configurations, the Hartree-Fock energies are in the continuum of He $1s2p^3P^o$. Thus, the excitation $2p \rightarrow \sigma_{2p}$ gives rise to an open-channel correlation effect which represents a truly continuum component ($1s2p\epsilon p$) which cannot be treated accurately as localized correlation, i.e., in terms of square-integrable functions only.^{14,15} The rest of the clusters in Eq. (1) represent wave packets above the $1s2p^2$ HF energy and therefore, they can be expressed in terms of square-integrable functions and computed variationally subject to orthogonality constraints to the HF $1s$ and $2p$ orbitals.

Since the structure of electron correlation for 4P and 2P is the same (see the Appendix) and since the HF energy of 4P is below that of 2P by 0.130 eV, the computational emphasis was put on the 4P state.

The localized correlation was expressed in terms of one, two, and three symmetrized orbital excitations. The corresponding virtual orbitals were optimized by minimizing the full configuration-interaction energy. For the pair excitations $2p^2 \rightarrow v_1^2$, the terms up to $l=4$ were computed explicitly. The corresponding CI correlation energy is 0.2852 eV. For the remaining portion of the $2p^2$ correlation, we found an l^{-6} dependence, in agreement with our previous work⁹ on the $2p^2^3P$ two-electron systems. Using the computed angular correlation energies up to $l=4$ and the value of the Riemann zeta function for $\zeta(6) = \sum_{K=1}^{\infty} K^{-6} = 1.01734306$, we obtained for the remaining of the angular pair correlation of the $2p^2$ pair,

$$\sum_{l=5}^{\infty} \epsilon_{2p^2}(l) = -0.00026 \text{ eV}.$$

Therefore, the total localized correlation energy for the 4P was found to be -0.2855 eV (1 a.u. = 27.2079 eV).

The open-channel electron correlation was computed by mixing the HF $1s2p^2^4P$ function with the continuum of the HF $1s2p^3P^o + \epsilon p$ scattering functions. This mixing causes a negative energy shift. The interaction between the localized correlation and the continuum was neglected because (1) the description of the 4P state by the HF function is very good (the HF coefficient is 0.95) and (2) inclusion of the localized correlation would reduce the magnitude of the shift, thus placing the 4P state even higher.

Unlike the well-known two-electron reorganization characteristic of ordinary autoionizing states, the type of interaction represented by the $1s2p^2 \rightarrow 1s2p\epsilon p$ mixing (and all similar cases of shape resonances) is more subtle and requires a different approach.

First, we compute Hartree-Fock functions for initial and final states separately. This yields nonorthonormal Hartree-Fock orbitals, $\overline{1s} \overline{2p}^2$ and $1s2p\epsilon p$. Then, the interaction matrix element is written as

$$W_{\epsilon}(E') = \langle 1s2p\epsilon p | H - E' | \overline{1s} \overline{2p}^2 \rangle \equiv V_{\epsilon} - E' S_{\epsilon}. \quad (2)$$

Using the HF equations for $\overline{1s} \overline{2p}^2$ and $1s2p\epsilon p$ and after some algebra, it can be shown that the matrix element V_{ϵ} is given in terms of the overlap S_{ϵ} and two R^K integrals which, however, turn out to be numerically negligible. Thus, Eq. (2) reduces to

$$W_{\epsilon}(E') = -(\epsilon - \epsilon_{2p}) S_{\epsilon}, \quad \epsilon' = E' - E_{\text{thresh}} \quad (3)$$

and the corresponding energy shift is

$$\Delta(\epsilon) = \mathcal{P} \int_0^{\infty} d\epsilon' \frac{|W_{\epsilon'}(\epsilon)|^2}{\epsilon - \epsilon'} \\ = (\epsilon - \epsilon_{2p})^2 \mathcal{P} \int_0^{\infty} d\epsilon' \frac{|S_{\epsilon'}|^2}{\epsilon - \epsilon'}, \quad (4)$$

where \mathcal{P} = principal value and

$$S_{\epsilon} \equiv \sqrt{2} \langle 2p/\overline{2p} \rangle \langle \epsilon p/\overline{2p} \rangle. \quad (5)$$

That is, for such shape resonances, mixing of bound with scattering states is due essentially to the different HF potentials and the resulting non-orthonormality.

Computation of Eq. (4) has yielded $\Delta = -0.0522$ eV. This is the largest of a series of values which were obtained by shifting the position of the localized wave function with respect to the threshold.

We also computed the shift taking into account localized correlation but representing the continuum approximately by square-integrable orbitals.^{14,15} The result from a total configuration-interaction calculation is -0.014 eV a much smaller value than the one obtained from the rigorous HF theory with scattering functions.

The relativistic energy was obtained using the experimental energy of He $1s2p^3P^o$ and the corresponding total nonrelativistic energy computed by Accad *et al.*¹⁶ We estimated $E_{\text{rel}} = -0.0026$ eV.

Adding the Hartree-Fock, correlation, and relativistic energies we obtained $E(^4P) = -58.0314$ eV which is above the experimental $E(\text{He } ^3P^o)$ by 0.01 eV. Since, as we stated before, the computed open-channel correlation is most probably larger than the true one, the 4P state is evidently unbound.

Given the analysis for the 4P state and the fact that for the 2P state electron correlation is similar, we conclude that the 2P state is definitely unbound and represents a core-excited shape resonance about 0.13 eV above the He $1s2p^3P^o$ threshold. Therefore, He^- has only two bound states: The $1s2s2p^4P^o$ at 19.74 eV and the $2p^3^4S^o$ at 59.33 eV (see the Appendix) above the He $1s^2^1S$ state. $^4S^o$ has still to be observed.

How do these states decay? They do so not only by autoionizing to the adjacent continua via the spin-dependent, relativistic forces which were considered in Refs. 1, 4 and 5, but also by *radiatively autoionizing* (RA)¹⁷ to the same continua. $^4S^o$ can decay via RA to the He $1s2p^3P^o$ -continuum nonrelativistically. We computed the total RA probability in the Hartree-Fock approximation to be $1.14 \times 10^{10} \text{ sec}^{-1}$. Electron correlation is not expected to change this by more than 20%. Similarly, we suggest that the $^4P^o$ state undergoes *relativistic radiative autoionization* by mixing via spin-dependent forces with the He $1s^2\epsilon p$ and $1s2s2p^2P^o$ continuum. The magnitude of such novel processes is presently unknown.

Figure 1 shows the discrete spectrum of He^- and the corresponding relevant He states. Also shown are the herein proposed *radiative* decay mechanisms.

III. CONCLUSION

He^- has two bound states. The $2p^3^4S^o$ is triply excited yet symmetry forces it to be part of the nonrelativistic spectrum. Our conclusion regarding the $1s2p^2^4P$ and 2P states is that they are not bound, a fact which renders the experimental

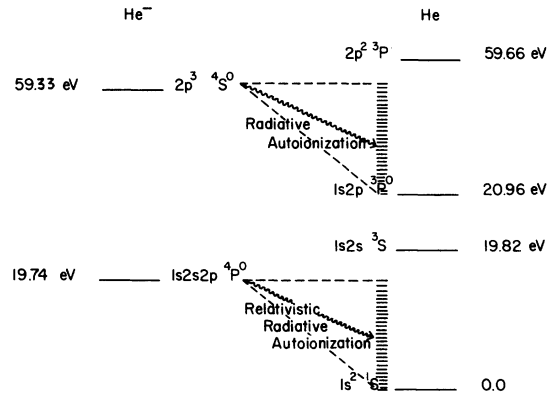


FIG. 1. The bound states and their radiative decay mechanisms of He^- (not in scale). These states can also undergo relativistic autoionization.

findings^{6,7} puzzling. The theoretically predicted extreme proximity of the 4P state to the He $1s2p^3P^o$ threshold should constitute a challenge for more theoretical and experimental laser work. A photoabsorption experiment from the metastable $\text{He}^- 1s2s2p^4P^o$ state which would record and correlate the appearance of the peak due to the $1s2p^2^4P$ configuration with the fluorescence of the He $1s2p^3P^o$ state could provide a definitive proof as regards the exact position of 4P .

Finally, we close by pointing out that, as the Bunge's^{10,11,18} and our work has shown, there are highly excited bound states in a number of negative ions. For example, a new system which has been examined computationally by us is the Be^- ion whose existence had thus far been an open question. We have found²⁰ that Be^- exists in three nonrelativistically bound states. These, together with those of the other ions, are given in Table I.

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TABLE I. The discrete spectra of certain negative ions.

H^{2-} Refs. 9 and 11	H^- Refs. 9 and 19	He^- Refs. 1, 9, 10, and this work	Li^- Ref. 18	Be^- Ref. 20
No bound state	$1s^2^1S$ $2p^2^3P$	$1s2s2p^4P^o$ $2p^3^4S^o$	$1s^22s^2^1S$ $1s^22s2p^2^5P$ $1s^22p^3^5S^o$	$1s^22s2p^2^4P$, $1s^22p^3^4S^o$ $1s2s2p^3^6S^o$

APPENDIX

Our electron correlation work on the $2p^3\ ^4S^o$ states of H^{2-} and He^- (Ref. 9) was not carried out to the limit because it became clear from a straightforward analysis that H^{2-} was unbound and He^- was bound. In view of the later work by Chung,⁹ we have recomputed the electron correlation of $He^- \ ^4S^o$. Using only an 18-vector function with optimized Slater-type orbitals, we obtained an electron affinity of 0.317 eV (Chung's result: 0.328 eV). The major correlation vectors are $2p^2 \rightarrow V_p^2$ (where V_p is an optimized virtual orbital of p symmetry), $2p^2 \rightarrow V_d^2$, $2p^2 \rightarrow V_f^2$, $2p \rightarrow V_p'$, and

the triple excitation $2p^3 \rightarrow V_p^3$. We note that in a number of *ground-state* calculations, triple excitations have previously been found to be always small. However, our results indicate that for diffuse, excited states this need not be due to strong second- and higher-order effects.

We have also studied approximately the $2p^2$ correlation of the $1s2p^2\ ^2P$ configuration. As predicted in the text, it is not sufficient to make it bound. Using a 10-vector, optimized function, we found that $\epsilon_{\text{corr}}(2p^2) \approx 0.20$ eV which is in good agreement with the trend established for such states in Ref. 9 of $\epsilon_{\text{corr}}(2p^2) \approx 0.25$ eV.

*Address for the academic year 1980–81: Physics Department, Amherst College, Amherst, Massachusetts 01002.

†Present address: Physics Department, Michigan Technological University, Houghton, Michigan 49931.

¹E. Holóien and S. Geltman, *Phys. Rev.* **153**, 81 (1967).

²Y. M. Demkov and G. F. Drukarev, *Zh. Eksp. Teor. Fiz.* **47**, 918 (1964) [*Sov. Phys. JETP* **20**, 614 (1965)].

³B. Brehm, M. A. Gusinow, and J. L. Hall, *Phys. Rev. Lett.* **19**, 737 (1967).

⁴G. N. Estberg and R. W. LaBahn, *Phys. Rev. Lett.* **24**, 1265 (1970).

⁵L. M. Blau, R. Novick, and D. Weinflash, *Phys. Rev. Lett.* **24**, 1268 (1970).

⁶R. A. Baragiola and E. R. Salvatelli, *J. Phys. B* **8**, 382 (1975).

⁷K. F. Dunn, B. J. Gilmore, F. R. Simpson, and H. B. Gilbody, *J. Phys. B* **11**, 1797 (1978).

⁸V. I. Safronova and V. S. Senashenko, *Phys. Lett.* **55A**, 401 (1976).

⁹D. R. Beck and C. A. Nicolaides, *Chem. Phys. Lett.* **59**, 525 (1978); K. T. Chung, *Phys. Rev. A* **20**, 724 (1979).

¹⁰A. V. Bunge and C. F. Bunge, *Phys. Rev. A* **19**, 452

(1979).

¹¹C. F. Bunge and A. V. Bunge, *Int. J. Quantum Chem.* **S12**, 345 (1978).

¹²D. R. Beck and C. A. Nicolaides, *Int. J. Quantum Chem.* **S14**, 323 (1980).

¹³D. R. Beck and C. A. Nicolaides, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Boston, 1978), p. 105.

¹⁴C. A. Nicolaides and D. R. Beck, *Int. J. Quantum Chem.* **14**, 457 (1978).

¹⁵C. A. Nicolaides, *Phys. Rev. A* **6**, 2078 (1972).

¹⁶Y. Accad, C. L. Pekeris, and B. Schiff, *Phys. Rev. A* **4**, 516 (1971).

¹⁷C. A. Nicolaides and D. R. Beck, *Phys. Rev. A* **17**, 2116 (1978).

¹⁸C. F. Bunge, *Phys. Rev. A* **22**, 1 (1980).

¹⁹G. W. F. Drake, *Phys. Rev. Lett.* **24**, 126 (1970).

²⁰D. R. Beck, C. A. Nicolaides, and G. Aspromallis (unpublished). The wavelength and transition probability of the $Be^- \ ^4S^o - ^4P$ transition are 2671 Å and $0.69 \times 10^9 \text{ sec}^{-1}$, respectively. The lifetime of the $^4S^o$ state is expected to be shorter by about 10% due to radiative autoionization into the $Be \ 1s^2 2s 2p \ ^3P^o$ continuum.