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Bound excited states of H^- and He^- in the statically screened Coulomb potential

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The stability of the bound excited states of both the hydrogen and helium anions in an environment represented by the statically screened Coulomb potential have been studied. Energies have been calculated at the full configuration interaction level of theory, as a function of the screening parameter. Our calculations demonstrate that the bound excited states of both H^- and He^- survive only under mild screening conditions. Stronger screening will yield a sequential electron detachment process. Finally, the applicability of the present calculations to model real plasmas is discussed. [S1050-2947(98)09904-1]

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I. INTRODUCTION

The concept of a rare gas anion goes against the grain of basic chemical concepts. When in their ground state, these atoms are closed shell systems and as such have no readily available low energy orbitals in which to place an extra electron. Thus, rare gas atoms are routinely considered incapable of binding an extra electron in their ground state electronic configuration [1]. Although some serious doubts have been recently raised [2] on the nonexistence of anion bound states in the gases Ar, Kr, and Xe, the statement holds strictly valid for the He and Ne [3]. However, when one considers excited states of these neutral atoms, the closed-shell argument no longer holds and the interesting possibility of a rare gas anion bound state arises.

In particular, the only two bound states [4] of He^- are excited bound states; namely, the $(1s2s2p)$ ^4P state, first suggested by Hiby [5], and the $(2p^3)$ ^4S state predicted by Beck and Nicolaides [6]. Both states have been observed experimentally and their energies with respect to the $(1s2s)$ ^3S state [7] and the $(2p^2)$ ^2P state [8,9] of the helium atom, respectively, measured rather accurately.

The stability of the bound excited states of atomic negative ions is a subject of considerable importance in many areas of physics, including electron scattering in atomic gases [10] and studies on the opacity in stellar atmospheres [11]. Most of the research done up until now has considered ions placed in a vacuum, but recently significant advances have been made in the study of polyelectronic atomic [12–17] and molecular systems [16,17] in environments represented by the statically screened Coulomb potential. Such screened potentials are important for many areas of physics, e.g., plasmas [18,19], nuclear and elementary particle physics [20], atomic physics [21], solid state physics [22], and atomic collision physics [23]. Thus it is to provide data concerning the intriguing H^- and the He^- anions and their properties under physically relevant conditions that we present the following study on the stability of the bound excited states of these atomic negative ions in such an environment.

II. METHODS

We adopt a full configuration interaction (FCI) approach to calculate all the various electronic states of interest of our polyelectronic Hamiltonian operator.

$$\hat{H}=\hat{T}+\hat{V} \tag{1}$$

with

$$\hat{T}=\sum_i \frac{-\nabla_i^2}{2} \tag{2}$$

and

$$\hat{V}=-Z\sum_i \frac{e^{-\lambda r_i}}{r_i}+\sum_{i>j}\frac{e^{-\lambda r_{ij}}}{r_{ij}}, \tag{3}$$

where λ is the screening parameter, r_i is the distance between the electron and nucleus of charge Z, and r_{ij} is the distance between electrons i and j. The details of FCI can be found elsewhere [24]. As usual, the wave function will be expanded as a linear combination of configurational state function built with a finite set of k spin orbitals $\{\chi_a\}_{i=1}^k$. The χ_a spin orbitals are now expanded in terms of Gaussian basis set functions, for which a closed-form analytical solution for all the required basis integrals is available [25]. Finally we have made sure that all the calculated wave functions satisfy the quantum mechanical virial theorem for the interaction potential of Eq. (3), namely,

$$2\langle\hat{T}\rangle=-\langle\hat{V}\rangle+\lambda\left[Z\left\langle\sum_i e^{-\lambda r_i}\right\rangle-\left\langle\sum_{i>j}e^{-\lambda r_{ij}}\right\rangle\right], \tag{4}$$

where $\langle\hat{O}\rangle$ stands for the quantum mechanical average of the operator $\hat{O}$ over the electron coordinates.

All the calculations have been performed with a locally modified version of the GAMESS [26] suite of programs, which includes the screened basic molecular integrals package [25].

III. RESULTS AND DISCUSSION

Building a basis function set flexible enough to characterize properly bound excited states of atomic negative ions is critical in arriving at meaningful results. Table I shows the FCI energies of the $(2s2p)$ ^3P and $(2p^2)$ ^3P states of H^-

TABLE I. Total energies in a.u. for the $(2s2p)$ ^3P and $(2p^2)$ ^3P excited states of the hydrogen anion and the $(2p)$ ^2P state of the hydrogen atom with various basis sets. The basis sets are identified by their number of s-, p-, d-, and f-type sets of basis functions (first, second, third, and fourth numbers of the first column, respectively). The s- and p-type sets were constructed starting from the $9s3p$ uncontracted basis set of Siegbahn and Liu [39] augmented with two sets of p-type function with exponents 3.0 and 9.0 times that of the greatest p-type exponent. Complementary basis functions, with exponents sequentially 1/3 times that of the most diffuse one of each type, were added until the given size was reached. The d- and f-type exponents were chosen to form an even-tempered set with ratio 3.0, starting from 0.372 145 and 1.0, respectively.

	H^-		H
Basis set	$(2s2p)$ ^3P	$(2p^2)$ ^3P	$(2p)$ ^2P
10/10/5/2	-0.141990	-0.125248	-0.124972
10/11/5/2	-0.141991	-0.125279	-0.124972
10/12/5/2	-0.141991	-0.125281	-0.124972
13/13/5/2	-0.142012	-0.125281	-0.124972
15/12/5/2	-0.142109	-0.125281	-0.124972
Exact	-0.142597[a]	-0.125355[b]	-0.125000

[a] Taken from Ref. [27].

[b] Taken from Ref. [30].

and the $(2p)$ ^2P state of H, calculated with various basis sets of increasing size. Recall that the $(2p^2)$ ^3P state of H^- is the only bound excited state of this species [4]. It is well known [27] that this state can decay radiatively into the $(2s2p)$ ^3P autoionization state. This transition gives rise to a line [28] of frequency 3784 cm^{-1}. Our best basis set calculation with the 15/12/5/2 basis set predicts a line at 3693 cm^{-1}, which is only slightly better than the prediction of the 10/12/5/2 basis set, namely 3667 cm^{-1}, but at a considerably larger computational cost. Furthermore, the 10/12/5/2 basis set yields only slightly poorer relative energies than both 15/12/5/2 and 13/13/5/2 basis sets for the $(2s2p)$ ^3P and the $(2p^2)$ ^3P states of H^- with respect to the $(2p)$ ^2P state of the hydrogen atom, as can be inferred from the data given in Table I. Hence, hereafter, all calculations on the hydrogen anion will be carried out with the 10/12/5/2 basis set, which constitutes a reasonably well balanced basis set for studying trends of the transition energies between the $(2s2p)$ ^3P and $(2p^2)$ ^3P states of H^- in the statically screened Coulomb potential.

TABLE III. Relative energies in eV between the $(1s2s)$ ^3S state of He and the $(1s2s2p)$ ^4P state of He^-, $\Delta E(^3S\text{-}^4P)$, the $(2p^2)$ ^3P state of He and the $(2p^3)$ ^4S of He^-, $\Delta E(^3P\text{-}^4S)$, and the $(2p^3)$ ^4S and $(1s2s2p)$ ^4P states of He^-, with various basis sets.

Basis set	$\Delta E(^3S\text{-}^4P)$	$\Delta E(^3P\text{-}^4S)$	$\Delta E(^4S\text{-}^4P)$
7/6/5	0.0650	0.3257	39.5956
7/7/5	0.0704	0.3260	39.6007
7/7/5/3	0.0710	0.3378	39.5869
Ref. [42]	0.0774		
Ref. [33]		0.3200	
Ref. [32]	0.0775	0.3410	39.59
Present work	0.0775	0.3417	39.59
Experiment	0.07767 ± 0.00012[a]	0.337 ± 0.025[b]	

[a] Taken from Ref. [7].

[b] Taken from Ref. [8].

Calculations on the bound excited states of He can also be carried out at a high level of accuracy without using prohibitively large basis sets. Table II collects the energies of the $(1s2s2p)$ ^4P and $(2p^3)$ ^4S excited states of He^- and the $(1s2s)$ ^3S and $(2p^2)$ ^3P excited states of the neutral He atom calculated with various basis sets of increasing size. Inspection of Table II reveals that the convergence toward the exact energy is slow but steady, with respect to the increase of the basis set size, a behavior exhibited also by ground state energies [29]. However, throughout a wide range, these basis sets do well in predicting relative energies. In Table III are shown various relevant relative energies among the states taken into consideration. It is readily seen that the three best basis sets yield a consistent overall high quality prediction. Since the 7/6/5 basis set balances well the computational cost and accuracy, subsequent calculations on the helium system were carried out with this basis set.

TABLE II. Total energies in a.u. for the $(1s2s2p)$ ^4P and the $(2p^3)$ ^4S bound excited states of the helium anion and the $(1s2s)$ ^3S and $(2p^2)$ ^3P excited states of the helium atom with various basis sets. The basis sets follow the same notation as in Table I. They were constructed starting from the standard 311G$(3pd)$ basis [40], 3/3/1 in our notation, and then complementary basis functions, with exponents sequentially 1/3 times that of the most diffuse one of each type, were added until reaching the given size.

	He^-		He	
Basis set	$(1s2s2p)$ ^4P	$(2p^3)$ ^4S	$(1s2s)$ ^3S	$(2p^2)$ ^3P
6/6/5	-2.174663	-0.720520	-2.173903	-0.709230
7/6/4	-2.174667	-0.720583	-2.173905	-0.709227
7/6/5	-2.176309	-0.721197	-2.173921	-0.709228
7/7/4	-2.174989	-0.720603	-2.173905	-0.709230
7/7/5	-2.176510	-0.721210	-2.173922	-0.709347
7/7/5/3	-2.176551	-0.721759	-2.173942	-0.709347
Exact	-2.178077[a]	-0.723058[b]	-2.175229[c]	-0.710500[c]

[a] Taken from Ref. [32].

[b] Taken from Ref. [41].

[c] Taken from Ref. [28].

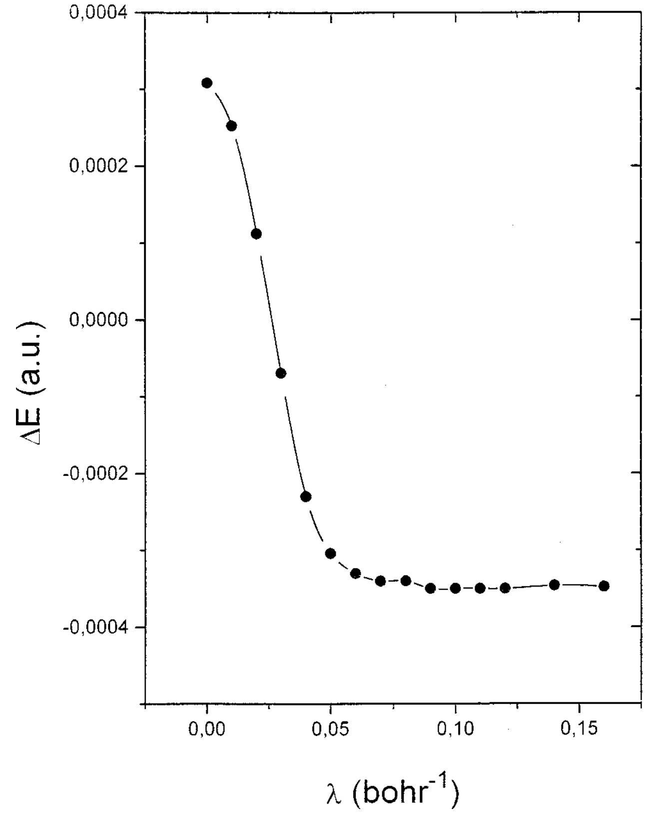

FIG. 1. Electron detachment energy, ΔE, in a.u. of the $(2p^2)$ ^3P state of H^- with respect to the $(2p)^2P$ state of H, as a function of the screening parameter, λ in bohr^{-1}.

A. The stability of the $(2p^2)$ ^3P state of H^-

The best approximation to the stability of the $(2p)$ ^3P bound state of H^- with respect to the $(2p)$ ^2P state of H, its electron affinity, for the unscreened case is 9.65 meV [30]. Our FCI calculation with the 10/12/5/2 basis set gives a value of 8.39 meV. Although our prediction is not in exact accord with the number of Jauregui and Bunge [30], it represents a good starting point for the investigation of the effect of the statically screened potential on the stability of this $(2p^2)$ ^3P bound excited state of H^-.

Screening of the Coulomb interactions within the atom yields weaker bound electrons, so that for sufficiently large screening, electron detachment might take place. We have calculated the electron detachment energy from the $(2p^2)$ ^3P state of H^- to the $(2p)$ ^2P state of H, as a function of the screening parameter. Results are depicted in Fig. 1, which shows that the detachment energy of one $2p$ electron of H^- decreases rapidly as the screening parameter increases. Indeed, for $\lambda \geqslant 0.03$ bohr^{-1} the $(2p)$ ^2P state of the neutral hydrogen atom is more stable than the $(2p^2)$ ^3P state of H^-, and for $\lambda \geqslant 0.07$ bohr^{-1} the energy difference between both states remains almost constant. Recall that the hydrogen atom is able to support a bound $(2p)$ ^2P state only for $\lambda \leqslant 0.22$ [31]. Below this critical value of $\lambda = 0.22$ bohr^{-1}, the energy difference between the $(2s2p)$ ^3P autoionization state and the $(2p^2)$ ^3P bound excited state of H^- decreases as λ increases, as shown in Fig. 2. Consequently the transition between these two states should give rise to lines of shorter wave numbers as the screening parameter increases. Indeed, at $\lambda = 0.03$ bohr^{-1}, where the stability of the $(2p^2)$ ^3P state of H^- becomes critical with respect to the $(2p)$ ^2P state of H, the predicted wave number for the $(2s2p)$ $^3P \rightarrow (2p^2)$ ^3P transition of H^- is 3516 cm^{-1}, 151 cm^{-1} shorter than in vacuum.

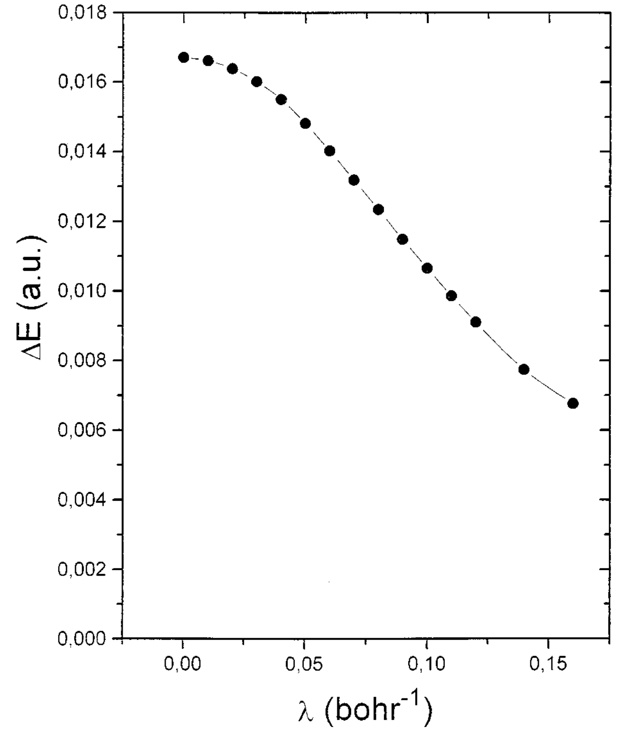

FIG. 2. Energy difference, ΔE, in a.u. between the $(2p^2)$ ^3P and the $(2s2p)$ ^3P states of H^- as a function of the screening parameter, λ in bohr^{-1}.

This loss of the one outer electron followed by loss of a second electron at a higher value of λ is in contrast to the behavior of the ground state H^- anion under the influence of screening [13,14,17]. In the ground state of H^-, the two electrons become unbound at *essentially* the same value of λ. Thus for the ground state of H^- sequential electron loss, as predicted in this work for the $(2p^2)$ ^3P bound excited state of H^-, is not seen, rather both electrons are lost under equal conditions.

B. The stability of the $(1s2s2p)$ ^4P state of He^-

Of the two bound excited states of He^-, the ^4P is the most stable one. It has an experimental [7] electron affinity, with respect to the $(1s2s)$ ^3S state, of 0.077 67 ± 0.000 12 eV, which compares well with our prediction of 0.0650 eV. The calculated total energy for the unscreened $(\lambda = 0)$ case is $-2.176\,309$ a.u. Hence, the basis set incompleteness, with respect to the exact energy of Bylicki and Pestka [32], is of 1.76×10^{-3} a.u., for our 7/6/5 basis set.

The stability of this ^4P state of He^- with respect to the $(1s2s)$ ^3S state of He is found to be a steadily decreasing function of the screening parameter. More interestingly, at $\lambda = 0.052$ bohr^{-1}, its stability becomes critical and for larger values of λ the $(1s2s)$ ^3S state of He is found to be more stable that the ^4P of He^-, as shown in Fig. 3. Therefore, the ^4P bound excited state of He^- is not able to support a bound state for the $2p$ outer electron for $\lambda > 0.052$ bohr^{-1}. At these higher λ values, He^- will lose this outer electron due to

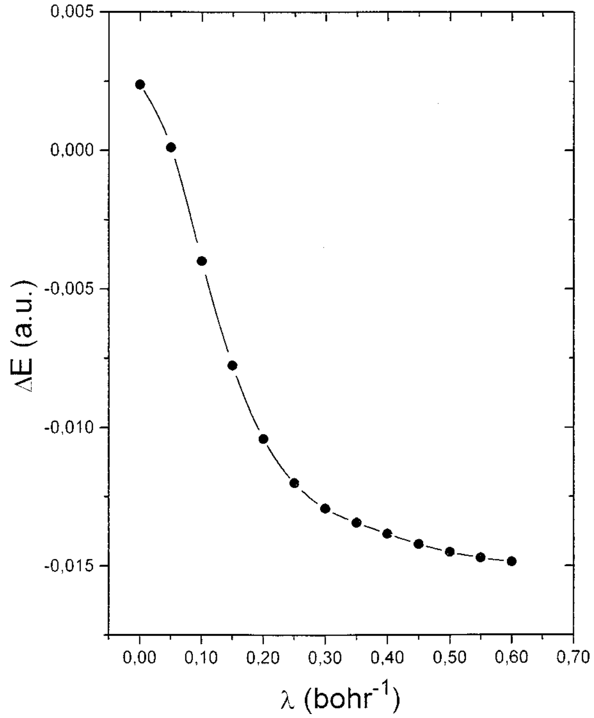

FIG. 3. Electron detachment energy, ΔE, in a.u. of the $(1s2s2p)$ ^4P state of He$^-$ with respect to the $(1s2s)$ ^3S state of He, as a function of the screening parameter, λ in bohr^{-1}.

pressure ionization (or any other plausible decay mechanism [33]).

It should be mentioned that the $(1s2s)$ ^3S excited state of the He atom may also be pressure ionized, as a consequence of the screening effect, yielding $(1s)$ ^2S He$^+$ and a detached electron. Our calculations predict that this should occur for $\lambda = 0.406$ bohr^{-1}, which is considerably larger than the corresponding critical λ for the pressure ionization of the $(1s2s2p)$ ^3P excited state of the He$^-$. Therefore the energy picture from our calculation is that electrons will be pressure ionized consecutively from the $(1s2s2p)$ ^4P bound excited state of the helium anion as a consequence of increasing the screening parameter.

C. The stability of the $(2p^3)$ ^4S state of He$^-$

The $(2p^3)$ ^4S state is a loosely bound excited state of He$^-$. Indeed, it has a total energy of only $-0.723\,058$ a.u. [32], a third of the ^4P state's energy. Its electron affinity with respect to the $(2p^2)$ ^3P state of 0.337 ± 0.025 eV [8,9] is also substantially lower than that of the ^4P state. Our predictions for the total energy and the electron affinity are $-0.721\,197$ a.u. and 0.326 eV, respectively, which compare well with respect to a number of earlier calculations [32,34]. In this case, the basis set incompleteness of our 7/6/5 basis set is 1.86×10^{-3} a.u., very similar to that of the ^4P state.

Figure 4 displays the energy of the $(2p^3)$ ^4S state of He$^-$ with respect to the $(2p^2)$ ^3P of He. It shows clearly that the ^4S state is stable only for small values of the screening parameter. For $\lambda > 0.183$ bohr^{-1}, the ^4S state of He$^-$ is less stable than the $(2p^2)$ ^3P state of He, implying that increasing beyond this value the screening will result in the detachment of an electron from He$^-$.

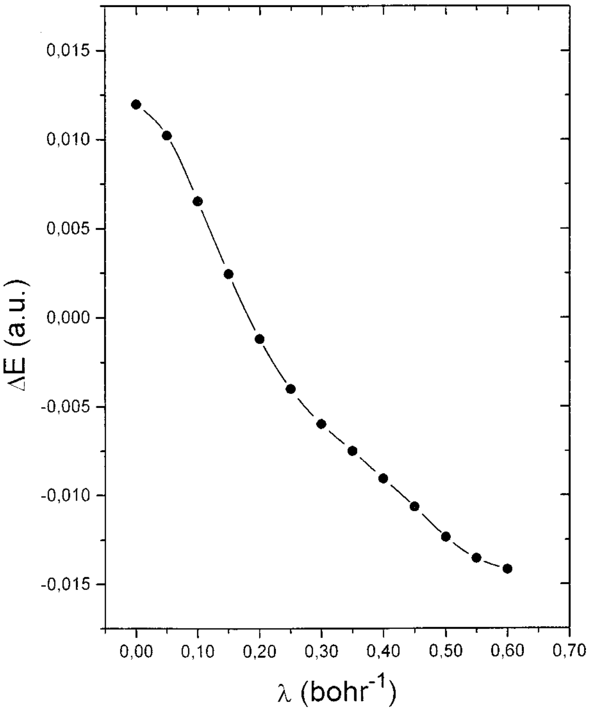

FIG. 4. Electron detachment energy, ΔE, in a.u. of the $(2p^3)$ ^4S state of He$^-$ with respect to the $(2p^2)$ ^3P state of He, as a function of the screening parameter, λ in bohr^{-1}.

The $(2p^2)$ ^3P excited state of the neutral helium atom will lose an electron by pressure ionization at values of $\lambda > 0.360$ bohr^{-1}. At that point, the $(2p^1)$ ^2P state of the He$^+$ cation is more stable than the ^3P neutral atom. However, the resulting $(2p)$ ^2P state of the He$^+$ is highly unstable, and at $\lambda > 0.45$ bohr^{-1}, the binding energy of its sole electron becomes negative. Therefore, similarly to the $(1s2s2p)$ ^4P state, the electrons of the $(2p^3)$ ^4S excited state of He$^-$ will be lost sequentially as a consequence of increasing the screening parameter.

IV. CONCLUSIONS

The bound excited states of H$^-$ and He$^-$ anions have been calculated at the full configuration-interaction level of theory, when both electrons and nuclei interact with each other through the statically screened Coulomb potential. The spin orbitals have been expanded in terms of Gaussian basis functions, for which fully analytical solutions for the molecular integrals involved in the self-consistent field problem are available. The quality of the resulting optimum FCI wave function has been verified with the aid of the quantum mechanical virial theorem.

Our calculations indicate that the bound excited states of both H$^-$ and He$^-$ survive only at small values of the screening parameter. For larger values of the screening parameter, electrons will be stripped off sequentially. This is in contrast to the behavior of the ground state H$^-$ and the neutral He, which lose their two electrons at essentially the same screening potential.

The hydrogen anion is predicted to lose one $2p$ electron from its $(2p^2)$ ^3P bound excited state for $\lambda \geqslant 0.03$ bohr^{-1}. Remarkably, the less stable bound excited state of the helium

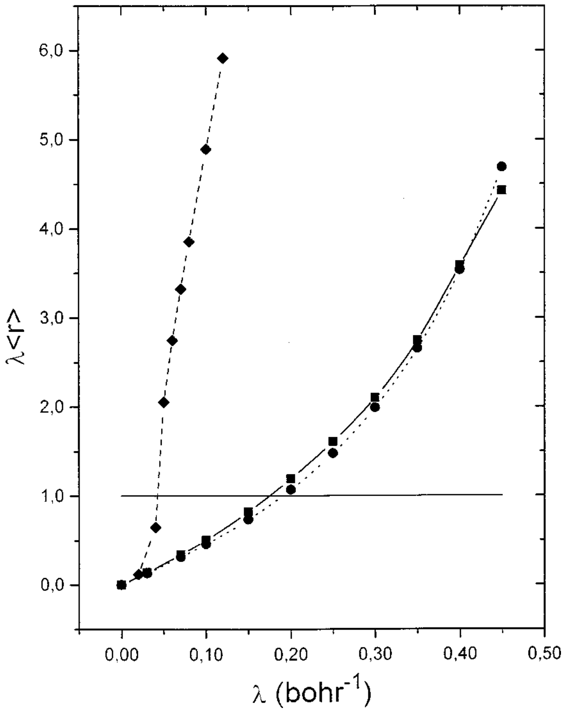

FIG. 5. The average nucleus-electron distance, $\langle r\rangle$ in bohr, multiplied by the screening parameter, λ in bohr^{-1}, for the $(1s2s2p)$ ^4P (solid line) and the $(2p^3)$ ^4S (dotted line) states of He$^-$ and the $(2p^2)$ ^3P state of H$^-$ (dashed line), versus the screening parameter, λ in bohr^{-1}.

anion, i.e., its $(2p^3)$ ^4S state, is predicted to survive stronger screening than the most stable $(1s2s2p)$ ^4P bound excited state. The former is predicted to pressure ionize at $\lambda=0.183$, while the latter at $\lambda=0.052$ bohr^{-1}.

The screened Coulomb potential has been used earlier to gain insight into various aspects of both laboratory and astrophysical plasmas [35], for screening is one salient feature of the collective behavior of plasmas [36]. However, since the actual form of the screened potential is derived by assuming equilibrium conditions and a thermal energy much larger than the potential energy $\langle\hat{V}\rangle$, which allows for the linearization of the Poisson equation, the interpretation of the results must be exercised with caution. Indeed, it is well established that the screened Coulomb potential describes plasma conditions reliably [37,38] only when the screening length, i.e., λ^{-1}, is larger than the average electron-nucleus distance, $\langle r\rangle$, so that the Debye sphere contains a large number of ions. As shown in Fig. 5, the $(1s2s2p)$ ^4P bound excited state of He$^-$ satisfies this condition for $\lambda<0.175$, and the $(2p^3)$ ^4S for $\lambda<0.190$ bohr^{-1}. Since the detachment of one electron from these states of helium anion takes place at lower λ values, one can conclude that the present model yields a feasible description of the stability of these bound excited states under plasma environments characterized by the screened Coulomb potential.

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