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Binding of an electron by He and Xe

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A recent theoretical paper [Guo, Wrinn, and Whitehead, Phys. Rev. A **40**, 6685 (1989)] predicted the existence of ground-state bound negative ions of all the noble gases. In addition, experimental observations [Haberland, Kolar, and Reiners, Phys. Rev. Lett. **63**, 1219 (1989)] suggest the existence of long-lived Xe^-. We have examined the cases of He^- and Xe^-. For He^-, we employed Levinson's theorem in conjunction with published and reliable theoretical e-He elastic-scattering phase-shift results. For Xe^-, we employed electron-correlation theory in conjunction with multiconfigurational Hartree-Fock and variational bound-state calculations of total energies. We conclude that these ions do not exist in a ground configuration.

A recent theoretical article [1] contains the prediction that all the noble gases, from Rn to He, have stable negative ions in the ground configuration, (atom) $ns\,^2S$. This conclusion is based on computational results from an application of a generalized local-spin-density functional theory (GLSDFT), in the nonrelativistic (NR) as well as in a quasirelativistic (QR) approximation, yielding electron affinities (EA's) ranging from 0.073 eV for He to 0.171 eV for Rn. Both the NR and QR calculations [1] yielded positive EA's. In quantitative terms, the relativistic effects changed the EA's of Xe from 0.112 to 0.124 eV and of Rn from 0.116 to 0.171 eV (Table II of Ref. [1]).

Since these predictions run counter to current electronic-structure theory and to experience with computations of small EA's, it is important to determine the degree of their validity.

If the GLSDFT [1] is so accurate and reliable (the EA's are computed as differences of statistical total energies), much of the accumulated knowledge from advanced polyelectronic theories on the importance of the details of interelectronic interactions and of relativity to achieve accuracies of 0.1–0.3 eV should be reexamined critically. Furthermore, if these predictions were correct, a previously unappreciated or unrecognized binding mechanism for the additional electron should be operating, since the combined result of quantities such as Coulomb repulsion, exchange interaction, and ns-core correlation based on a theory that starts with Hartree-Fock functions would seem inadequate. In that case, if an s electron could bind to a noble gas —especially He and Ne, whose Fermi sea [2–5] is totally closed and has no low-lying empty orbitals—then it would certainly bind to atoms throughout the Periodic Table with more polarizable or with open-shell zeroth-order structures.

The predictions of Guo, Wrinn, and Whitehead [1] have one possibly corroborating experimental observation, published recently [6]. A long-lived Xe^- ion was detected, with a lifetime longer than 10^{-4} s, but without an assignment of its state. In other words, it could correspond to a ground configuration or to an exceptionally long-lived metastable bound excited state [7].

In this paper we report the results of our analysis of the serious question that the two recent articles [1,6] have posed, i.e., the existence or not of ground-state negative ions of the noble gases. We studied two cases, "$1s^22l$" He^- and "$5p^66l$" Xe^- ($l=0,1,2,3$). Our conclusion is that they do not exist.

There is a variety of computational methods and a number of results that have been published on the subject of EA's. It is outside the scope of this paper to present an analysis of their rigor, generality, and efficiency, and therefore of their suitability for treating the problem of deciding whether an electron actually binds on the ground state of the noble gases. However, we point out that the reliable prediction of EA's must depend on a theoretical approach that combines all the necessary ingredients of electronic-structure-dependent electron correlation and scattering theory. These criteria are particularly relevant to the problem at hand [8].

Given the formal and practical problems associated with the above statement, in the quest for a definitive answer we applied two methods.

For He^-, we drew our conclusion from the existing information on e-He low-energy elastic scattering [9] and from the use of Levinson's theorem (see Ref. [5], p. 156),

which relates the number of bound states of the potential formed by the e-He interaction to the phase shift at zero energy [$\delta_0(0)=n\pi$, where n is the number of bound states]. This choice utilizes the fact that the scattering calculations on the compact He atom can be based on wave functions representing reality accurately, so that there can be no doubt as to the reliability of the prediction based on Levinson's theorem. On the other hand, one might be less easily convinced about the rigor of such a zero-energy scattering calculation on the polyelectronic, and hence difficult to treat accurately, Xe^- — even if it were available. Thus, in this case we opted for a bound-state approach, by analyzing electron correlation and computing the electron affinity as the energy difference $E(N)-E(N+1)$ [7].

The results of Duxler, Poe, and Labahn [9] have been obtained at three levels of approximation: static exchange, adiabatic exchange, and polarized orbitals. It is clear from the results—and well known to the experts—that the phase shift at $E=0$ goes to π, and that any improvement due to additional correlation effects cannot change this fact.

A phase shift of π implies that the e-He interaction creates only one bound level, the "1s." However, since the He $1s^2$ shell is occupied, this result does not lead to a physical state of He^-. Therefore, since no other one-electron bound solution exists, the He^- "$1s^2 2s\ ^2S$" state is unbound.

From the scattering calculations of the $l=1,2$ phase shifts [9], which go to zero as $E\rightarrow 0$, the same conclusion is drawn from the higher-l configurations.

As regards Xe^-, we followed the approach described in Refs. [2] and [7]. First, we aimed at obtaining converged solutions for Xe^- at a quasimulticonfigurational Hartree-Fock (MCHF) level [10] satisfying the virial theorem, the correct number of nodes, and reasonable orbital energies. These criteria were adopted [11] as necessary constraints for the zeroth-order establishment of localization of diffuse quasibound states, which are found in the continuous spectrum.

By a combination of analytic and numerical orbital techniques, we obtained results showing that the additional electron *cannot* bind in an s orbital. This conclusion is in agreement with that of Haberland, Kolar, and Reiners [9], which was based on elastic-scattering data.

Next we looked at higher electron momenta. We ran a series of small MCHF calculations for the $5s^25p^66p\ ^2P^\circ$, $5d\ ^2D$, and $4f\ ^2F^\circ$ configurations in the presence of configurations such as $5s5p^65d6p$, $5s5p^64f5d$, and $5s^25p^56p^2$ for $^2P^\circ$, $5s^25p^45d^3$, $5s5p^65d^2$, and $5p^65d^3$ for ^2D, and $5p^64f^3$, and $5s^25p^54f^2$ for $^2F^\circ$, which are expected to stabilize the lowest root and constrain the outer electron from running away. We searched for solutions with realistic average values of r for the outer electron (up to 15 a.u.). From this search, only the $^2P^\circ$ configuration yielded a physically meaningful HF solution with $\langle r\rangle_{6p}=7.2$ a.u. and an energy 2.6 eV above the HF energy of Xe $5p^6\ ^1S$. We then computed the $(5p6p)\ ^{3,1}S$, $^{3,1}P$, $^{3,1}D$ and the $(5s6p)\ ^{3,1}P^\circ$ pair-correlation energies together with the contributions of the single orbital excitations $5s\rightarrow d$, $5p\rightarrow f$, and $6p\rightarrow p$ [2,7], all of which are absent from the correlation of the neutral state. This calculation yields a differential energy that is about 1.6 eV, i.e. much smaller than the 2.6-eV difference of the HF energies. Due to the electronic structure of the $Xe^-\ ^2P^\circ$ and Xe ^1S configurations, what is left of the differential correlation energy cannot make up for this remainder [12].

In summary, our analysis of the problem of the existence or not of ground-state bound negative ions of noble gases, which was raised by two recent papers [1,6], leads to the conclusion that, according to our bound-state calculations and to published scattering calculations [9] in conjunction with Levinson's theorem, they do not exist. (Although only two were examined, the smallest and a large one, the essential physics must apply to the others as well.) On the one hand, this conclusion is not surprising. On the other hand, given the recently published predictions of very small electron affinities by the local-spin-density functional theory on systems such as the noble gases [1] or the alkaline earths [13], it appears that a more critical appraisal of this theory and its capabilities would be useful.

Finally, given the open question of the existence of Xe^- in a long-lived bound excited state, we [14] will report our results from calculations of relativistic autoionization [7,15,16] elsewhere, as soon as they are conclusive.

[1] Y. Guo, M. C. Wrinn, and M. A. Whitehead, Phys. Rev. A **40**, 6685 (1989).

[2] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. **S8**, 17 (1974); in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1978), p. 105.

[3] C. A. Nicolaides and D. R. Beck, in *Excited States in Quantum Chemistry* (Ref. 2), p. 143.

[4] The "Fermi sea" of zeroth-order orbitals and related configurations for atoms was introduced in Refs. [2] and [3] with the purpose of obtaining a better qualitative and quantitative description of zeroth-order electronic structure and properties throughout the Periodic Table. According to this idea, only He and Ne are truly closed systems. The rest of the noble gases are pseudoclosed, and this explains drastic differences in their physical properties such as the following: (1) A jump in the *polarizabilities* from Ne to Ar, something which a statistical theory does not predict (see comment on p. 151 of Ref. [3]); (2) a different *chemical reactivity* behavior for the heavy noble gases; (3) the existence of the cross-section minimum in the *Ramsauer-Townsend effect* in slow electron Ar,Kr,Xe elastic scattering, which is *absent* in the elastic scattering from He or Ne (see Ref. [5], p. 562); (4) different features and correlation effects in the *photoabsorption cross sections* due to the presence of zeroth-order configurations in initial and final states made up of vacant Fermi-sea orbitals (Ref. [3]).

[5] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon, Oxford, 1965).

[6] H. Haberland, Th. Kolar, and Th. Reiners, Phys. Rev. Lett. **63**, 1219 (1989).

[7] For a recent review and new results on the energetics and dynamics of bound excited states of atomic negative ions, see C. A. Nicolaides, G. Aspromallis, and D. R. Beck, J. Mol. Struct. (Theochem.) **199**, 283 (1989).

[8] One should not dismiss the fact of the existence of the neutral-atom continuous spectrum and its possible role in the function space in terms of which the zeroth order or the correlated $\psi(N+1)$ are expressed and computed. For example, a bound-state-type variational calculation for $E(N+1)$ may end up yielding the energy of atom plus electron at infinity, whether or not the negative ion exists. On the other hand, if the theory is based on a zeroth-order Hartree-Fock (HF) or multiconfigurational HF bound solution for $\psi(N+1)$, things are simplified if it is found that it has converged properly, regardless of whether the final result yields a positive or a negative EA. As test cases of the above comments, consider the simplest of negative ions, H^- and He^-. For H^-, the restricted HF bound solution exists, although it yields negative EA, i.e., an unbound H^- ^1S state. This is corrected when a calculation of electron correlation is carried out in terms of a function space which implicitly or explicitly contains the contribution of the continuous spectrum. On the other hand, the HF equations do not produce a converged bound solution for He^- "$1s^2 2s$" ^2S. This negative result implies that we are faced with a problem where the neutral-atom continuous spectrum must somehow enter in the computation as an energetically accessible scattering function space. [Even when a HF bound solution exists, there are situations of very small EA's which require the careful incorporation of the effects of the continuum in order to distinguish between a bound state and a shape resonance. See C. A. Nicolaides, Y. Komninos, and D. R. Beck, Phys. Rev. A **24**, 1103 (1981), for the treatment of the He^- $1s2p^2$ ^4P shape resonance.]

[9] W. M. Duxler, R. T. Poe, and R. W. Labahn, Phys. Rev. A **4**, 1935 (1971).

[10] Such solutions serve in zeroth order in order to screen possible candidates and to estimate the major effects of electron correlation beyond MCHF.

[11] C. A. Nicolaides, Phys. Rev. A **6**, 2078 (1972); C. A. Nicolaides and D. R. Beck, Int. J. Quantum Chem. **14**, 457 (1978).

[12] It is important to note that in these electron correlation computations the $5s^2 5p^6$ core is "broken" so as to account for major core and core–nl-electron interactions. Breaking the core in a variational calculation of EA is in principle more correct. However, it may destroy the empirically determined predictive capacity of simpler calculations involving only valence electrons. For example, D. R. Beck, Z. Cai, and G. Aspromallis, Int. J. Quantum Chem. **S21**, 457 (1987) computed that the core effects on Sc^- $^1D^\circ$ lead to an unbound system, contrary to observation [C. S. Feigerle, Z. Herman, and W. C. Lineberger, J. Electron Spectrosc. **23** 441 (1981)]. At the same time, a valence-only calculation by G. H. Jeung, Phys. Lett. **113A**, 73 (1985), yields a bound species. Similar comments can be made for the Ca^- $4s^2 4p$ $^2P^\circ$ prediction of C. Froese-Fischer, J. P. Lagowski, and S. H. Vosko, Phys. Rev. Lett. **59**, 2263 (1987) using valence-only MCHF. A recently published study of the core effects [P. Fuentealba, A. Savin, H. Stoll, and H. Preuss, Phys. Rev. A **41**, 1238 (1990)] shows significant core effects to the point that no decision on the Ca^- could be made.

[13] S. H. Vosko, J. B. Lagowski, and I. L. Mayer, Phys. Rev. A **39**, 446 (1989).

[14] G. Aspromallis and C. A. Nicolaides (unpublished).

[15] G. Aspromallis, C. A. Nicolaides, and Y. Komninos, J. Phys. B **18**, L545 (1985); G. Aspromallis, C. A. Nicolaides, and D. R. Beck, J. Phys. B **19**, 1713 (1986).

[16] G. Aspromallis and C. A. Nicolaides, J. Phys. B **19**, L13 (1986).