Theoretical study of even- and odd-parity states in La^- and Ac^-: Evidence for the uniqueness of La^-

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Density-functional-theory calculations predict that (i) La^- is a unique negative ion in that it has bound states of both even and odd parity in the configurations $[Xe]5d^26s^2$ and $[Xe]5d^16s^26p^1$, respectively, and (ii) the ground state of Ac^- is of odd parity in the configuration $[Rn]6d^17s^27p^1$ while the even-parity state $[Rn]6d^27s^2$ is unlikely to be bound. The dominant relativistic effects have been included perturbatively and are essential for these predictions.

In recent years it has become evident that most atoms, including those with closed subshells such as Ca, Sr, and Ba, can bind an extra electron to form a negative ion.[1-4] However, no negative ion has yet been identified with *bound* states relative to the neutral atom ground state (i.e., *stable* against autoionization) of both parities. Moreover, a study of the spectra of neutral and singly ionized atoms[5,6] shows that the energy separation between their ground and first excited states of opposite parity is greater than ~0.5 eV and thus is not close to being degenerate. The main purpose of this Brief Report is to present strong theoretical evidence that La^- is a unique system possessing both of these characteristics (i.e., nearly degenerate even- and odd-parity bound states in the configurations $[Xe]5d^26s^2$ and $[Xe]5d^16s^26p^1$). A system with such an electronic structure is likely to have unusual properties, e.g., a large electric dipole polarizability and Stark effect. It should also be useful in parity-nonconserving studies that have received much attention recently.[7]

On the basis of semiempirical (SE) analyses, the accepted view is that La^- and Ac^- are stable[1,8-12] in configurations $[Xe]5d^26s^2$ and $[Rn]6d^27s^2$, respectively, the latter with a very small binding energy (BE). La^- has been observed,[13] but no measurements of its quantum numbers have been reported. There have been no observations of Ac^-. Thus another unexpected result from our analysis is that the ground state of Ac^- is of odd parity in the configuration $[Rn]6d^17s^27p^1$ while the presently accepted[12] even-parity ground state, $[Rn]6d^27s^2$ (henceforth the noble-gas portion will be dropped), is unlikely to be bound.

There is experimental evidence[1,2] that once a bound configuration occurs in a column of the Periodic Table it usually is stable for all cases with higher atomic number below it (e.g., groups IIA and VA). This rule holds for negative ions even when the ground states of the neutral atoms in a column have different configurations, e.g., groups VB, VIB, and VIIIB. Thus noting the experimental discovery[14] of stable Sc^- and Y^- with the electron configurations $(n-1)d^1ns^2np^1$ ($n = 4$ and 5), it would be most unusual for La^- and Ac^- not to be bound in similar odd-parity states with $n = 6$ and 7. From this viewpoint our results for even-parity La^- (bound) and Ac^- (unbound) are most surprising. The real question that must be answered is what causes even-parity La^- to be different from the other group IIIB even-parity negative ions. In this respect, the SE analysis of the $(n-1)d^2ns^2$ configurations by Zollweg is noteworthy since it predicted an abrupt change[8] of the electron affinity (EA) in going from Sc^- and Y^- (unbound) to La^- (bound). However, the analysis gives very little insight into what causes La^- to be different from the others. A first-principles explanation of this anomalous behavior is given in the present work. To corroborate the validity of our conclusions, we show that the experimental *sd* interconfiguration energies (ICE's) of these elements have a similar anomaly for La and then combine these results with calculations to support our direct calculations for the EA's of the $(n-1)d^2ns^2$ states.

Our predictions are based on calculations of energy differences, $\Delta E \equiv E(A) - E(A^-)$, for the pertinent multiplets of the neutral atoms and negative ions. The energy of the nonrelativistic (NR) Hamiltonian is calculated using density-functional theory (DFT) to which the J-independent relativistic contributions (mass-velocity, Darwin terms, and spin-spin contact) are added perturbatively, denoted by $\Delta E_{\rm rel}$. The sensitivity of the relativistic contributions to d orbital occupancy makes them essential for producing the unique character of La^- as well as the observed ground-state configurations of La and Ac. Vosko, Lagowski, and Mayer[4] (VLM) found that relativity unbinds the $(n-1)d^1ns^2$ configurations in Ba^- and Ra^- ($n = 6$ and 7). VLM show that this perturbative treatment is adequate for p- and d-electron removal from neutral Sc, Y, La, and Ac by a comparison with Dirac-Hartree-Fock (DHF) calculations. This demonstration is extended to their negative ions in Table II.

The accurate determination of the NR ΔE is very difficult because of the importance of correlation in selecting the physical ground-state configuration due to its large fractional contribution to both the total binding energy and the "effective potential" that acts on the ex-

tra electron.[15] An example is the observed[14] odd-parity configuration in both Sc^- and Y^- where bound np orbitals do not exist in the Hartree-Fock (HF) approximation but do exist for the $(n-1)d$ orbitals in the unstable even-parity configurations. In the present work, this difficulty is overcome by using the HF-system method of DFT which includes correlation while maintaining the simple single-particle picture of HF theory. In this method, the NR ground-state energy is written as

$$E_v[n_\uparrow, n_\downarrow] = E_v^{\mathrm{HF}}[n_\uparrow, n_\downarrow] + E_c[n_\uparrow, n_\downarrow], \quad (1)$$

where $E_v^{\mathrm{HF}}[n_\uparrow, n_\downarrow]$ is the HF energy functional,[4] $E_c[n_\uparrow, n_\downarrow]$ is the correlation energy functional, and $n_\sigma(\mathbf{r})$ is the spin-up (-down) density for $\sigma = \uparrow$ ($\downarrow$). $E_v[n_\uparrow, n_\downarrow]$ is determined by minimizing it with respect to the $n_\sigma(\mathbf{r})$. An appealing feature of DFT is that the introduction of $E_c[n_\uparrow, n_\downarrow]$ in (1) combined with the variational principle for $E_v[n_\uparrow, n_\downarrow]$ results in the addition of a local single-particle correlation potential, $v_c(\mathbf{r})$, into the usual self-consistent single-particle HF equations, DFT-HF equations. The potential $v_c(\mathbf{r})$ is instrumental in binding relevant orbitals which are unbound in HF theory. The exact $E_c[n_\uparrow, n_\downarrow]$ is not known and must be approximated. With the recent verifications[2] of the DFT predictions[3,4] of stable Ca^-, Sr^- and Ba^-, it is evident that this method, with some of the presently available correlation energy functionals, is suitable for such systems. To show that it can also handle more complex systems such as La^- and Ac^- where there are two electrons outside of a closed subshell, it will be calibrated against the accurate experimental results for the multiplet structure[14] of Sc^- and Y^-. We have also tested the method for calculating energy differences in more relativistic systems and found it to be adequate for our purposes. Lagowski and Vosko[15] have analyzed five forms for $E_c[n_\uparrow, n_\downarrow]$ currently in use and found that the Stoll-Pavlidou-Preuss (SPP) form[16] underestimates the EA's of all negative ions with $Z < 30$. Also, it does not bind[4] the np states of Ca^-, Sr^-, and Ba^-. Thus it can be regarded as representing a lower limit to the true $E_c[n_\uparrow, n_\downarrow]$ for these problems and as such is useful for establishing the existence of stable negative ions. The results of the Perdew form[17] are also presented to give an example of a stronger $E_c[n_\uparrow, n_\downarrow]$ and verify that the even-parity states in Sc^-, Y^-, and Ac^- are not unstable just for the SPP form. The calculations were done using the general HF program[18] modified to include $v_c(\mathbf{r})$ and calculate E_v.

For the odd-parity configurations $(n-1)d^1ns^2np^1$, the possible multiplets are $^3F^o$, $^3D^o$, $^3P^o$, $^1F^o$, $^1D^o$, and $^1P^o$. Only the $^1D^o$ (ground state[14,19]) and $^3D^o$ have been observed in Sc^- with BE's of 6.95±0.73 and 1.54±0.73 and in Y^- with BE's of 11.32±0.44 and 6.06±0.92 (all energies are in mhartrees). Efforts were made to obtain converged solutions to the DFT-HF equations for all of the above multiplets using both the Perdew and SPP forms of E_c. The Perdew form gives bound converged solutions to the DFT-HF equations for all four ions in the $^3F^o$, $^3D^o$, and $^1D^o$ terms, while the SPP form

TABLE I. DFT results for the contributions to the BE's of the negative-ion states for Perdew and SPP functionals where $\Delta E_{\mathrm{tot}} \equiv \Delta E_{\mathrm{HF}}^{\mathrm{DF}} + \Delta E_c + \Delta E_{\mathrm{rel}}$ are compared with experimental (expt) and semiempirical (semi) values from Refs. 1, 12, and 14.

	Perdew	SPP	Perdew	SPP	Perdew	SPP	Perdew	SPP
Sc^-	$3d^14s^24p^1\ ^3F^o$		$3d^14s^24p^1\ ^3D^o$	$(1.54)^{\mathrm{expt}}$	$3d^14s^24p^1\ ^1D^o$	$(6.95)^{\mathrm{expt}}$	$3d^24s^2\ ^3F^e$	$(-28)^{\mathrm{semi}}$
$\Delta E_{\mathrm{HF}}^{\mathrm{DF}}$	−10.9		−10.2		−7.6	−6.4	−48.1	−47.4
ΔE_c	16.5		16.9		22.0	13.6	26.9	12.5
ΔE_{rel}	−0.3		−0.5		−0.3	−0.3	−4.5	−4.4
ΔE_{tot}	5.4		6.1		14.1	6.8	−25.6	−39.3
Y^-	$4d^15s^25p^1\ ^3F^o$	$(\sim 6)^{\mathrm{expt}}$	$4d^15s^25p^1\ ^3D^o$	$(6.06)^{\mathrm{expt}}$	$4d^15s^25p^1\ ^1D^o$	$(11.32)^{\mathrm{expt}}$	$4d^25s^2\ ^3F^e$	$(-17)^{\mathrm{semi}}$
$\Delta E_{\mathrm{HF}}^{\mathrm{DF}}$	−5.6	−4.8	−8.4		−2.7	−1.6	−26.2	−25.5
ΔE_c	17.0	5.7	16.7		22.5	14.1	25.8	11.0
ΔE_{rel}	−0.4	−0.5	−1.6		−0.8	−0.7	−11.4	−11.2
ΔE_{tot}	11.0	0.4	6.6		19.1	11.8	−11.8	−25.7
La^-	$5d^16s^26p^1\ ^3F^o$		$5d^16s^26p^1\ ^3D^o$		$5d^16s^26p^1\ ^1D^o$		$5d^26s^2\ ^3F^e$	$(19)^{\mathrm{semi}}$
$\Delta E_{\mathrm{HF}}^{\mathrm{DF}}$	−2.9	−2.5	−4.2	−2.7	1.3	1.7	25.6	25.8
ΔE_c	16.9	5.9	17.2	6.4	22.2	13.7	26.0	10.7
ΔE_{rel}	−1.4	−1.5	−3.2	−2.9	−1.8	−1.8	−25.0	−24.9
ΔE_{tot}	12.6	1.8	9.8	0.8	21.6	13.5	26.6	11.6
Ac^-	$6d^17s^27p^1\ ^3F^o$		$6d^17s^27p^1\ ^3D^o$		$6d^17s^27p^1\ ^1D^o$		$6d^27s^2\ ^3F^e$	$(11\pm11)^{\mathrm{semi}}$
$\Delta E_{\mathrm{HF}}^{\mathrm{DF}}$	−1.2	−1.0	−1.5	−1.4	1.7	3.3	31.6	31.5
ΔE_c	16.8	5.8	17.0	6.4	22.0	13.5	25.6	10.4
ΔE_{rel}	−2.8	−3.2	−7.0	−6.9	−4.3	−4.1	−55.5	−55.3
ΔE_{tot}	12.7	1.5	8.5	−1.9	19.4	12.7	1.6	−13.4

failed to do so for the ^{3}F° and $^3D^o$ terms in Sc^- and the ^{3}D° term in Y^- emphasizing its characteristic weak v_c. To obtain ΔE, the neutral-atom energies were calculated for the experimental ground states $(n-1)d^1ns^2\,{}^2D^e$. The results for the ΔE's are summarized in Table I along with those for the $(n-1)d^2ns^2\,{}^3F^e$ term. The importance of correlation and relativity in producing binding or unbinding is shown by separating ΔE_v into a "density-functional HF" part, $\Delta E_{\rm HF}^{\rm DF}$, and a correlation part, ΔE_c, which are compared to $\Delta E_{\rm rel}$.

A study of the results for Sc^- and Y^- in Table I shows that DFT captures the major physics and is in reasonable agreement with experiment. Namely, the $^1D^o$ is their ground state and since it is favored by $\Delta E_{\rm HF}^{\rm DF}$, it would persist if a more accurate $E_c[n_\uparrow, n_\downarrow]$ was available. (We have found that $\Delta E_{\rm HF}^{\rm DF}$ favors the $^1D^o$ state in each of the five forms for $E_c[n_\uparrow, n_\downarrow]$ discussed in Ref. 15.) The agreement between the SPP form and the $^1D^o$ experiments is particularly good. Thus it is natural to extend this form to La^- and Ac^-. The Perdew form can be calibrated against Sc^- and Y^- by subtracting ~7.5, resulting in BE's of 14.1 and 11.9 for La^- and Ac^-, which are in close agreement with SPP. Even if the $\Delta E_{\rm rel}$ is more negative by 2 (see VLM's Table V), La^- and Ac^- would still be stable in the $^1D^o$ state. Therefore we are confident that the $^1D^o$ state is bound in both La^- and Ac^- and is their lowest-energy odd-parity state.

The interpretation of the $^3D^o$ results is more difficult because the discrepancies between the Perdew form values and experiment are markedly different in Sc^- and Y^-. However, any reasonable calibration of the Perdew form would bind the $^3D^o$ state in La^- and Ac^- with a smaller BE than the $^1D^o$ state. This conclusion is supported by the existence of converged solutions of the DFT-HF equations with the SPP form for La^- and Ac^- with very small and negative, respectively, BE's. The situation for the $^3F^o$ state is unclear because it is very unlikely to be bound in Sc^- and a definitive identification in Y^- is yet to be made.[14,20] If it exists in Y^-, its BE is expected to be[14,20] 6±1. Since each form of E_c gives very similar BE's for Y^-, La^-, and Ac^- (although depending on the form of E_c), we conclude that if the $^3F^o$ state is bound in Y^- then it is bound in La^- and Ac^- with a similar BE.

The results for the $^3F^e$ state in Table I are in qualitative agreement with the SE analyses[8,12] except for Ac^- where our results strongly suggest it to be unstable (note the SE result[12] is 11±11, so that the disagreement is not so severe) leaving La^- as the only stable even-parity system. This unique property is produced by the competition of two opposing contributions: The $\Delta E_{\rm HF}^{\rm DF}$ makes an abrupt change in sign (negative to positive) in going from Sc and Y to La and Ac. The $\Delta E_{\rm rel}$ is always negative but rapidly becomes more so in going from Sc to Ac (by a factor of ~12). The net result is that $\Delta E_{\rm HF}^{\rm DF} + \Delta E_{\rm rel}$ is positive only for La. When the nearly constant positive ΔE_c is added, it produces substantial binding in La, but is not large enough to reverse the negative contribution of $\Delta E_{\rm rel}$ for Ac. Since $\Delta E_{\rm rel}$ is so important for this special property, the accuracy of the perturbative treatment is corroborated by comparing it with DHF calculations[21] (see Table II). The special feature of Ac^- is already evident in that converged DHF solutions for $^3F^e$ do not exist for the real nuclear charge $Z = 89$ (i.e., Ac^-'s result is extrapolated from higher Z). The accuracy of $\Delta E_{\rm rel}$ can be seen by comparing it with $\Delta E_{\rm rel}^{\rm DHF}$ ($\equiv \Delta E_{\rm tot}^{\rm DHF} - \Delta E_{\rm HF}$), the maximum discrepancy being ~2.

TABLE II. A comparison of ΔE's for a $(n-1)d$ electron removal from $^3F^e$ using DHF and HF + perturbative $E_{\rm rel}$.

	Sc^-	Y^-	La^-	Ac^-
$\Delta E_{\rm HF}$	−46.9	−25.1	26.3	32.1
$\Delta E_{\rm rel}$	−4.4	−11.2	−24.6	−54.7
$\Delta E_{\rm rel}^{\rm DHF}$	−5.3	−11.9	−25.5	−56.4[a]

[a]Extrapolated from Z =89.1, 89.08, 89.06, 89.04 to Z =89.0.

The abrupt change in the BE of the $^3F^e$ state in going from La^- to Ac^- is so unexpected that it deserves corroboration (since the available $E_c[n_\uparrow, n_\downarrow]$'s are not as reliable[15] for d electron removal (as can be seen from the larger spread of ΔE_c between Perdew and SPP for $^3F^e$). Independent evidence, based on analysis of experimental data, that La is special will now be presented. The neutral-atom experimental $(2J+1)$ averaged s-d ICE's, $\Delta E_{sd}^{\rm expt} \equiv E[(n-1)d^2ns^1\,{}^4F^e] - E[(n-1)d^1ns^2\,{}^2D^e]$, are compared with the DFT-HF results in Table III. From the $\Delta E_{sd}^{\rm expt}$ it is clear that La is special in that it can accommodate two d electrons much more readily than the others. This property is reproduced by the DFT-HF calculations albeit with substantial errors in the Perdew form. Because the SPP errors for ΔE_{sd} are smaller we favor its results for the $^3F^e$ term in Table I. It is important to appreciate that this special property of La is due to the same opposing contributions discussed above, namely, $\Delta E_{\rm HF}^{\rm DF}$ and $\Delta E_{\rm rel}$ whose values are not in doubt and are insensitive ($\lesssim$10%) to the inclusion of v_c in the DFT-HF equations. (Note the sign change in Tables I and III because we are using

TABLE III. Comparison of experimental (Refs. 5 and 6) with DFT-HF results for $s-d$ ICE's, ΔE_{sd}.

	Sc	Y	La	Ac
$\Delta E_{sd}^{\rm expt}$	52.4	49.9	13.1	43.4
$\Delta E_{\rm HF}^{\rm DF}$	37.6	16.2	−35.1	−40.2
$\Delta E_c^{\rm Perdew}$	4.0	6.3	2.8	2.7
$\Delta E_{\rm rel}$	4.7	13.2	26.2	58.8
$\Delta E_{sd}^{\rm tot}$	46.3	35.8	−6.1	21.3
$\Delta E_{\rm HF}^{\rm DF}$	37.4	15.8	−35.6	−41.2
$\Delta E_c^{\rm SPP}$	15.9	18.7	14.9	14.7
$\Delta E_{\rm rel}$	4.7	13.1	26.1	58.3
$\Delta E_{sd}^{\rm tot}$	58.0	47.7	5.4	31.8

the standard definition of ΔE_{sd}.) $\Delta E_{sd}^{\text{expt}}$ can be used to give a qualitative explanation as well as a more reliable estimate of the BE's of the ${}^3F^e$ term. Instead of adding an $(n-1)d$ electron to the ${}^2D^e$ ground state, add an ns electron to the ${}^4F^e$ excited state with BE $\Delta E_{ns} \equiv E[(n-1)d^2ns^1\,{}^4F^e] - E[(n-1)d^2ns^2\,{}^3F^e]$. If $\Delta E_{ns} - \Delta E_{sd}^{\text{expt}} > 0$, the ${}^3F^e$ state will be stable. Thus for La^- to be stable ΔE_{6s} must be greater than 13 while for the others it must be on the order of 45 to 55. An estimate of ΔE_{ns} for $n = 4$, 5, and 6 can be obtained from the experimental[1] EA's of K^-, Rb^-, and Cs^- (18.4, 17.9, and 17.3) (Ref. 22) which are nearly constant,[23] suggesting that the ΔE_{ns}'s corresponding to Sc^-, Y^-, La^-, and Ac^- are nearly constant and greater than 17 which is sufficient to make ${}^3F^e$ La^- stable. To put this picture on a more quantitative basis, DFT results for ΔE_{ns} are presented in Table IV. If we use the average values for ΔE_{ns} combined with $\Delta E_{sd}^{\text{expt}}$, we arrive at BE's of -33, -27, 6, and -23 for the ${}^3F^e$ state of Sc^-, Y^-, La^-, and Ac^-. Since this picture avoids the errors in $E_c[n_\uparrow, n_\downarrow]$ for d-electron removal we believe these values to be our best estimates for these BE's with an uncertainty[22] of ≈ 4.

In summary our results predict the following: (i) La^- and Ac^- have the bound odd-parity states ${}^1D^o$ (BE in the range 10–15), ${}^3D^o$ (BE in the range 5–8) and likely ${}^3F^o$ (BE in the range 4–8); (ii) only La^- has a bound even-parity ${}^3F^e$ state (BE in the range 4–10). It should be emphasized that these BE's are estimates only. The important aspect of our predictions is that La^- has nearly degenerate stable states of both parities which is likely to produce interesting physics. Because of the delicate nature of these systems, careful experimental studies will be necessary to confirm our predictions. It is hoped that this theoretical analysis will stimulate such work.

TABLE IV. BE's of ns electrons in the ${}^3F^e$ state, ΔE_{ns}.

	Sc^-	Y^-	La^-	Ac^-
$\Delta E_{\text{HF}}^{\text{DF}}$	−10.5	−10.0	−9.5	−8.6
$\Delta E_{\text{c}}^{\text{Perdew}}$	30.9	32.1	28.8	28.3
ΔE_{rel}	0.2	1.8	1.2	3.3
ΔE_{ns}	20.7	24.0	20.5	22.9
$\Delta E_{\text{HF}}^{\text{DF}}$	−10.0	−9.7	−9.8	−9.7
$\Delta E_{\text{c}}^{\text{SPP}}$	28.4	29.7	25.6	25.1
ΔE_{rel}	0.3	1.9	1.2	3.0
ΔE_{ns}	18.7	22.0	17.0	18.4

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[22] The DFT-HF values of these EA's for the Perdew (19.6, 18.7, 18.8) and SPP forms (15.4, 14.8, 14.0) bracket the experimental values and give an indication of the accuracy of the corresponding ΔE_{ns}.
[23] Unfortunately, an EA for Fr^- is unavailable. However, the ionization potentials of Ca, Sr, Ba, and Ra are similarly nearly constant (i.e., 224.6, 209.3, 191.5, and 194.0).