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### Prediction of stable $\text{Sr}^-$ , $\text{Ba}^-$ , and $\text{Ra}^-$ from density-functional theory

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Density-functional theory calculations using the Hartree-Fock system method provide strong theoretical evidence that the negative ions  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$  are stable in the ground states with the odd-parity configurations  $ns^2np$  ( $n=4,5,6$ ). The dominant relativistic effects have been included perturbatively and are essential in choosing these configurations instead of  $(n-1)dns^2$  in  $\text{Ba}^-$  and  $\text{Ra}^-$ .

In a recent Letter, Froese Fischer, Lagowski, and Vosko<sup>1</sup> (henceforth referred to as FFLV) predicted that  $\text{Ca}^-$  is stable in the electron configuration  $[\text{Ar}]4s^24p$ . Although there was some tenuous evidence<sup>2</sup> that  $\text{Ca}^-$  might be stable, it was generally accepted to be unstable<sup>3</sup> and this configuration was completely unanticipated. The conclusion that  $\text{Ca}^-$  is stable was based on multiconfiguration Hartree-Fock (MCHF) and density-functional theory (DFT) calculations and has been confirmed in an elegant experiment by Pegg, Thompson, Compton, and Alton.<sup>4</sup> FFLV were led to consider this unexpected electron configuration from the experimental study of  $\text{Sc}^-$  and  $\text{Y}^-$  by Feigerle, Herman, and Lineberger<sup>5</sup> who found that they each had two bound states with the unexpected electron configurations  $[\text{Ar}]3d4s^24p$  and  $[\text{Kr}]4d5s^25p$ , respectively. These electron configurations are unusual because in nearly all stable negative ions<sup>3</sup> there are at least two electrons in the valence subshell (the other exception is  $\text{Pd}^-$ ). A natural question is whether this type of electron configuration persists for the ground states of negative ions for higher atomic number,  $Z$ , in groups IIA and IIIB elements.

The purpose of this Communication is to present theoretical evidence based on DFT calculations for the existence of the stable ions  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$  in the electron configurations  $[\text{Kr}]5s^25p$ ,  $[\text{Xe}]6s^26p$ , and  $[\text{Rn}]7s^27p$ . With respect to  $\text{Sr}^-$ , it should be noted that from an MCHF calculation, Froese Fischer<sup>6</sup> recently predicted that  $\text{Sr}^-$  is stable with an electron affinity (EA) of 0.11 eV in the ground-state configuration  $[\text{Kr}]5s^25p$ . The present Communication presents further support for this prediction. We have also considered the possibility of adding an electron in a  $d$  orbital to the neutral atoms (i.e., the negative-ion configurations  $[\text{Kr}]4d5s^2$ ,  $[\text{Xe}]5d6s^2$ , and  $[\text{Rn}]6d7s^2$ ) and have found none of these configurations to be stable although bound nonrelativistic wave

functions were found to exist for the latter two. [Henceforth, the rare-gas closed shells will be dropped and the valence-electron configurations will be denoted by  $ns^2np$  and  $(n-1)dns^2$ .] According to the presently available experimental data<sup>3</sup>  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$  are regarded as unstable. The theoretical evidence for these odd-parity bound states is based on calculations of the ground-state energies and the EA's using DFT for the above electron configurations. The existence of such stable negative ions conforms with the trend that once a stable negative ion exists in a group, the elements with larger atomic number are also stable<sup>3</sup> (e.g., groups VA and VIIB). The viewpoint taken in this paper is that  $\text{Ca}^-$  serves as a direct demonstration of the adequacy of the DFT to predict the stability of such ions.

The usual starting point for theoretical investigations of atomic systems is the Hartree-Fock<sup>7</sup> (HF) approximation which accounts for more than 99% of the total energy. However, for the above configurations the HF method does not produce converged solutions with the  $np$  or  $(n-1)d$  orbital bound. To overcome this difficulty, the more powerful density-functional theory is used which has the capacity to include correlation, while maintaining the single-particle picture of HF theory. In particular, the so-called HF-system method of DFT (Refs. 8 and 9) is used because it is essential to have complete cancellation of the self-Coulomb interaction in the Hartree and the exchange terms when dealing with negative ions. Also, on the basis of the usual quantum-mechanical variational principle the HF energies calculated from the DFT [henceforth referred to as HF (DFT) energies] themselves provide rigorous upper bounds for the energies (independent of DFT) which in most atomic systems agree with the true ground-state configurations<sup>10</sup> and thus give a reliable indication of what the true ground-state configurations are for the negative ions under consideration.

TABLE I. The DFT results for the various contributions to total energy and their corresponding differences,  $\Delta E = E(A) - E(A^-)$  (in hartrees) for Ca and  $\text{Ca}^-$ . The electron affinity (Ref. 4) is 0.0016.

	Ca $4s^2^1S$	$\text{Ca}^- 4s^2 4p^2P$
$E_{\text{HF}}(\text{DFT})$	-676.7574	-676.7462
$E_c^P$	-0.8694	-0.8857
$E_v$	-677.6268	-677.6319
$E_{\text{rel}}$	-2.7807	-2.7804
$E_{\text{tot}}$	-680.4075	-680.4123
$\Delta E_{\text{HF}}(\text{DFT})$		-0.0112
$\Delta E_c^P$		0.0163
$\Delta E_v$		0.0051
$\Delta E_{\text{rel}}$		-0.0004
$\Delta E_{\text{tot}}$		Electron affinity = 0.0048

According to the Hohenberg-Kohn<sup>11</sup> theorems (i) the ground-state energy may be written as

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

where  $E_v^{\text{HF}}[n_{\uparrow}, n_{\downarrow}]$  is the HF energy functional and  $E_c[n_{\uparrow}, n_{\downarrow}]$  is the correlation energy functional<sup>9</sup> and (ii)  $E_v[n_{\uparrow}, n_{\downarrow}]$  must be minimized with respect to the spin densities  $n_{\sigma}(r)$  ( $\sigma = \uparrow$  and  $\downarrow$  for spin-up and -down number densities, respectively). The introduction of the correlation energy functional in (1) combined with the variational principle for  $E_v[n_{\uparrow}, n_{\downarrow}]$  results in the addition of a correlation potential into the usual self-consistent single-particle HF equations. If the exact  $E_c[n_{\uparrow}, n_{\downarrow}]$  were known and if any of the negative ions  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$  were stable, then the inclusion of the correlation potential would prevent the autoionization of the extra electron from the ground-state orbital, which occurs in the HF theory. In fact, the exact  $E_c[n_{\uparrow}, n_{\downarrow}]$  is not known and thus must be approximated. Lagowski and Vosko<sup>10</sup> (henceforth referred to as LV) have analyzed the five correlation energy functionals<sup>12</sup> currently in use and have found that the Kohn-Sham (KS), Vosko-Wilk (VW), and Perdew forms are capable of a few millihartrees accuracy for calculating the EA's when the extra electron goes into a  $2p$  or a  $3p$  orbital while the Langreth-Mehl-Perdew-Hu (LMPH) form overestimates the correlation energy con-

TABLE II. Results for Sr and  $\text{Sr}^-$ . The MCHF electron affinity (Ref. 6) is 0.0040. (See Table I for notation.)

	Sr $5s^2^1S$	$\text{Sr}^- 5s^2 5p^2P$
$E_{\text{HF}}(\text{DFT})$	-3131.5448	-3131.5359
$E_c^P$	-2.0746	-2.0905
$E_v$	-3133.6194	-3133.6264
$E_{\text{rel}}$	-43.6949	-43.6937
$E_{\text{tot}}$	-3177.3142	-3177.3201
$\Delta E_{\text{HF}}(\text{DFT})$		-0.0088
$\Delta E_c^P$		0.0159
$\Delta E_v$		0.0071
$\Delta E_{\text{rel}}$		-0.0012
$\Delta E_{\text{tot}}$		Electron affinity = 0.0059

tribution and thus is not useful for establishing stability. Evidence of the adequacy of these  $E_c[n_{\uparrow}, n_{\downarrow}]$  for the  $d$  orbitals under consideration will be given below.

The calculations have been performed with the general HF program<sup>13</sup> modified to include the correlation potential, and Eq. (1) was used to evaluate the total energies for all the above  $E_c[n_{\uparrow}, n_{\downarrow}]$ . Only the Stoll-Pavlidou-Preuss (SPP) form does not produce any bound  $np$  or  $(n-1)d$  orbitals (including the  $4p$  orbital of  $\text{Ca}^-$  which has been observed<sup>4</sup>). All the others produce bound  $np$  orbitals and positive EA's for  $\text{Ca}^-$ ,  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$ . Also, in  $\text{Ba}^-$  and  $\text{Ra}^-$  they produce bound  $(n-1)$  orbitals with positive removal energies when relativistic effects are ignored. We have chosen to present the numerical results for the Perdew form of  $E_c[n_{\uparrow}, n_{\downarrow}]$ , since it gives more accurate and smaller correlation energy contributions to the EA's in the  $3p$  shell than the local spin-density approximation<sup>8,9</sup> (i.e., the KS form) and thus it strengthens our conclusions concerning the stability of these negative ions. Also, the Perdew form has the potential for further improvements. It is worth mentioning that the VW form which underestimates the EA's for the  $2p$  and  $3p$  shells and gives an error of only 2.1 mhartrees for  $\text{Ca}^-$  produces positive EA's for  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$ .

It is well known (LV) that relativistic effects can make significant contributions (of similar magnitude to the non-relativistic HF and correlation energies) to the EA's for systems with  $Z > 20$ . To estimate such effects a perturba-

TABLE III. Results for Ba and  $\text{Ba}^-$ . (See Table I for notation.)

	Ba $6s^2^1S$	$\text{Ba}^- 6s^2 6p^2P$	$\text{Ba}^- 5d 6s^2^2D$
$E_{\text{HF}}(\text{DFT})$	-7883.5426	-7883.5361	-7883.5250
$E_c^P$	-3.3629	-3.3791	-3.3882
$E_v$	-7886.9055	-7886.9152	-7886.9132
$E_{\text{rel}}$	-228.1673	-228.1649	-228.1478
$E_{\text{tot}}$	-8115.0727	-8115.0801	-8115.0610
$\Delta E_{\text{HF}}(\text{DFT})$		-0.0065	-0.0176
$\Delta E_c^P$		0.0163	0.0253
$\Delta E_v$		0.0097	0.0077
$\Delta E_{\text{rel}}$		-0.0024	-0.0195
$\Delta E_{\text{tot}}$		Electron affinity = 0.0073	-0.0118

TABLE IV. Results for Ra and Ra<sup>-</sup>. (See Table I for notation.)

	Ra $7s^2 1S$	Ra <sup>-</sup> $7s^2 7p^2 P$	Ra <sup>-</sup> $6d 7s^2 2D$
$E_{\text{HF}}(\text{DFT})$	-23 094.3023	-23 094.2964	-23 094.2939
$E_c^P$	-6.0085	-6.0247	-6.0335
$E_v$	-23 100.3108	-23 100.3211	-23 100.3274
$E_{\text{rel}}$	-1530.8604	-1530.8548	-1530.8158
$E_{\text{tot}}$	-24 631.1712	-24 631.1759	-24 631.1432
$\Delta E_{\text{HF}}(\text{DFT})$		-0.0059	-0.0084
$\Delta E_c^P$		0.0162	0.0250
$\Delta E_v$		0.0103	0.0166
$\Delta E_{\text{rel}}$		-0.0057	-0.0446
$\Delta E_{\text{tot}}$		Electron affinity = 0.0046	-0.0281

tive<sup>13</sup> evaluation of the  $J$ -independent relativistic corrections (mass velocity, Darwin terms, and spin-spin contact) is included in the calculation of the total energy. This relativistic correction strongly favors the  $ns^2 np$  over the  $(n-1)dns^2$  configurations for the ground states of Ba<sup>-</sup> and Ra<sup>-</sup>. Unexpectedly, it reverses the order of the energy levels of the nonrelativistic calculation for Ra<sup>-</sup>.

The DFT results are presented in Tables I–IV. For both Ca<sup>-</sup> and Sr<sup>-</sup>, we were not able to obtain converged solutions for the  $(n-1)dns^2$  configurations. The calculated EA for Ca is 4.8 mhartrees (using the Perdew form for  $E_c[n_\uparrow, n_\downarrow]$ ) and thus overestimates the observed value by 3.2 mhartrees. It is important to note that even though the relativistic energy contribution to the EA,  $\Delta E_{\text{rel}}$ , is small (-0.4 mhartrees), it is an appreciable part of the experimental<sup>4</sup> (1.6 mhartrees) value and should be included. The calculated EA for Sr is 5.9 mhartrees and is in reasonable agreement with the MCHF (Ref. 6) result of 4 mhartrees. If the error in the DFT calculation is similar to that for Ca (i.e., too large by  $\sim 3$  mhartrees), then the Sr EA would still be positive ( $\sim 3$  mhartrees).

Tables III and IV summarize the results for Ba<sup>-</sup> and Ra<sup>-</sup>. For these cases the tables contain the corresponding calculations performed for the  $(n-1)dns^2$  configurations. These elements are especially interesting because the relativistic energy contribution chooses which of the configurations  $ns^2 np$  or  $(n-1)dns^2$  is the stable

ground state. In particular, purely on the HF (DFT) level, the  $ns^2 np$  configuration is favored to be the ground state for both Ba<sup>-</sup> and Ra<sup>-</sup>. However, the correlation energy contribution is significantly larger for the  $(n-1)dns^2$  configuration (by approximately 9 mhartrees for both elements) and its addition produces two bound states for both Ba and Ra. In the case of Ra<sup>-</sup> it unexpectedly reverses the HF energy levels with  $(n-1)dns^2$  configuration becoming the ground state. This picture is drastically changed when the relativistic energy contribution is included. For both Ba and Ra, the  $(n-1)dns^2$  configurations once again become unstable while the  $ns^2$  retain their positive EA's (7.3 and 4.6 mhartrees, respectively). Even though these values might be overestimated, as in the cases of Ca<sup>-</sup> and Sr<sup>-</sup> by a few ( $\sim 3$ ) mhartrees, the  $ns^2 np$  states would still remain bound. It should be noted from Table IV that the relativistic contribution reduces the nonrelativistic estimate of EA for Ra by 5.7 mhartrees. This reduction would be partially compensated by the spin-orbit interaction in a full relativistic calculation so that our best estimate for the EA of Ra is 4–5 mhartrees. Thus the conclusion is that both Ba<sup>-</sup> and Ra<sup>-</sup> are stable and similar to Ca<sup>-</sup> and Sr<sup>-</sup> in that their ground-state configurations are  $ns^2 np$  ( $n=6$  and  $7$ ). It is interesting to note that if this result is confirmed experimentally Ra<sup>-</sup> will be the first atomic system with a  $7p$  orbital occupied in the ground state.

Since the relativistic energy contribution plays such an important role in the calculations of EA's in Ba and Ra, we have done a test on the elements adjacent to the Ca, Sr, Ba, and Ra, i.e., the group IIIB elements Sc, Y, La, and Ac, to establish the adequacy of the perturbative

TABLE V. Comparison of the DF relativistic energy contributions to the  $np$  and  $(n-1)d$  electron removal energies with the perturbative results (see text for discussion). All energies in hartrees.

Element	$\Delta E_{\text{rel}}(\text{DF})$	$\Delta E_{\text{rel}}(\text{pert})$
Sc ( $4s^2 4p$ )	-0.0005	-0.0006
Y ( $5s^2 5p$ )	-0.0017	-0.0016
La ( $6s^2 6p$ )	-0.0029	-0.0027
Ac ( $7s^2 7p$ )	-0.0076	-0.0058
Sc ( $3d 4s^2$ )	-0.0070	-0.0068
Y ( $4d 5s^2$ )	-0.0158	-0.0155
La ( $5d 6s^2$ )	-0.0295	-0.0286
Ac ( $6d 7s^2$ )	-0.0662	-0.0611

TABLE VI. Comparison of the "experimental" correlation energy contribution to the  $(n-1)d$  electron removal energies with the DFT results (see text for discussion). All energies in hartrees.

Element	$\Delta \mathcal{E}_c^{\text{expt}}$	$\Delta \mathcal{E}_c^P$
Sc ( $3d 4s^2$ )	0.0275	0.0383
Y ( $4d 5s^2$ )	0.0318	0.0358
La ( $5d 6s^2$ )	0.0302	0.0351
Ac ( $6d 7s^2$ )	0.0294	0.0343

treatment for energy differences. In Table V we compare the  $(2J+1)$ -weighted Dirac-Fock<sup>14</sup> [ $\Delta E_{\text{rel}}(\text{DF})$ ] results with the perturbative [ $\Delta E_{\text{rel}}(\text{pert})$ ] calculations for the removal of  $d$  and  $p$  electrons from the configuration  $(n-1)dns^2$  and  $ns^2np$  in group IIIB. It can be seen that when the relativistic energy differences are compared, the largest error  $\sim 5$  mhartrees was obtained for the removal of the  $d$  electron from Ac and  $\sim 2$  mhartrees or less for the  $p$  electrons. These results are in agreement with the LV findings for elements with  $Z \leq 30$ . Thus, Table V supports our conclusion that the relativistic effects strongly favor the  $ns^2np$  configurations in the negative ions of group IIA. It is also worth noting that the magnitudes of the relativistic contributions are similar for corresponding elements and orbitals in groups IIA and IIIB.

There remains the question of the approximate  $E_c[n_{\uparrow}, n_{\downarrow}]$  accuracy for the  $d$  electron removal energies in  $\text{Ba}^-$  and  $\text{Ra}^-$ . In particular, do they underestimate the correlation energy contribution to these  $d$  electron removal energies to such an extent that the  $(n-1)dns^2$  configuration becomes the ground state? To this end we have compared the "experimental" correlation energy contribution  $\Delta \mathcal{E}_c^{\text{expt}}$  to the  $(n-1)d$  electron removal energies in the group IIIB elements with the DFT values in Table VI.  $\Delta \mathcal{E}_c^{\text{expt}}$  was calculated by subtracting the DF  $(n-1)d$  electron removal energy (including the spin-orbit coupling) from the experimental values<sup>15,16</sup> and  $\Delta \mathcal{E}_c^P = \Delta E_c - \Delta E_{\text{HF}}$  where  $E_{\text{HF}}$  is the HF energy without the correlation potential. The final states in  $\text{Y}^+$  and  $\text{Ac}^+$  are ground states while those in  $\text{Sc}^+$  and  $\text{La}^+$  are not. The main point to note from Table VI is that  $\Delta \mathcal{E}_c^P$  is larger

than  $\Delta \mathcal{E}_c^{\text{expt}}$ , i.e., it is not underestimated in these cases. However, because of the complexity of  $\Delta E_c$  one cannot definitely conclude that  $\Delta \mathcal{E}_c^P$  overestimates the analogous quantity in  $\text{Ba}^-$  and  $\text{Ra}^-$ . In fact, even  $\Delta \mathcal{E}_c^P$  is too small by 5 to 10 mhartrees for  $\text{Ba}^-$  and  $\text{Ra}^-$  (there is no evidence for this) the  $(n-1)dns^2$  configurations would not be stable when relativistic effects are included.

On the basis of the above results, we make the following conclusions: (i) The  $ns^2np$  configurations have lower energies than the  $(n-1)dns^2$  configurations in  $\text{Ba}^-$  and  $\text{Ra}^-$ , (ii) even if DFT overestimates the correlation energy contribution to EA's by  $\sim 3$  mhartrees (as in  $\text{Ca}^-$ )  $\text{Ba}^-$  and  $\text{Ra}^-$  would remain stable, and (iii)  $\text{Sr}^-$  is stable in agreement with the MCHF calculation of Froese Fischer.<sup>6</sup> In our view, the evidence presented is sufficiently strong that it warrants a substantial experimental effort to observe these negative ions, to measure their EA's, and determine their electron configurations.

*Note added in proof.* Since this work was submitted, evidence for the existence of stable  $\text{Ba}^-$  has been reported at the Tenth Conference on the Application of Accelerators in Research and Industry, Denton, Texas, 1988 by the IsoTrace Laboratory, University of Toronto [L. R. Kilius, M. A. Garwan, A. E. Litherland, M.-J. Nadeau, J. C. Rucklidge, and X.-L. Zhao, Nucl. Instrum. Methods B (to be published)].

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