Binding energies for p electrons in negative alkaline-earth elements

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Multiconfiguration Hartree-Fock (MCHF) calculations recently predicted a positive binding energy for the p electron in the $s^2p\ ^2P$ state of Ca$^-$, in good agreement with experiment. The present paper explores the binding of electrons in several alkaline-earth elements. Fixed-core Hartree-Fock potentials demonstrate the angular momentum barrier. From a simple correlation study it is shown that the $3d^24p$ configuration relative to the $3s^23p$ configuration in Mg$^-$ lies much higher than the $(n-1)d^2np$ configurations relative to ns^2np in the heavier alkaline-earth elements. Accurate MCHF correlation studies are reported for two and three electrons outside a core from which binding energies are predicted for Ca$^-$, Sr$^-$, and Ba$^-$. Not included is correlation with the core (core polarization) and correlation within the core. The same procedures were also applied to Sc. Theoretical results with relativistic shift corrections are compared with experiment in the case of Ca$^-$ and Sc.

I. INTRODUCTION

Most neutral atoms are able to bind an extra electron to form a stable negative ion, but the rare gases are well-known exceptions. The extensive survey on binding energies of negative ions by Hotop and Lineberger[1] shows that the alkali-metal elements acquire a second s electron to form stable s^2 states; the alkaline-earth elements are listed as having an electron affinity (EA) < 0, implying that a stable state of the negative ion does not exist. In the case of the light elements (Be, Mg, Ca), this conclusion was based on some theoretical calculations and semiempirical extrapolation, whereas for the heavier elements of Sr and Ba, the evidence was based entirely on extrapolation. The extensive calculations by Bunge et al.,[2] for elements up to Ca, were motivated largely by a study of metastable states rather than stable negative ion states and semiempirical extrapolation, at least isoelectronic extrapolation, requires a knowledge of the designation of the lowest state of the negative ion.

Recently, Pegg et al.[3] reported a positive electron affinity for Ca and identified the ground state of the negative ion as $4s^24p\ ^2P$. The identification agreed with the theoretical predictions of Froese Fischer et al.,[4] who used both a multiconfiguration Hartree-Fock (MCHF) method and a density-functional theory for their predictions. The MCHF electron affinity was in good agreement with experiment. The fact that the extra electron was a p electron, resulting in an odd-parity state, is counterintuitive. The spectrum of Ca$^-$ would be expected to be similar to that of Sc, where the ground state is $3d4s^2\ ^2D$ and the first excited state is $3d^2(^3F)4s\ ^4F$. Configurations involving d electrons, particularly pairs of d electrons, tend to be "plunging configurations" in that, as the effective nuclear charge increases, they rapidly descend to the lower levels of a spectrum. Alternatively, as the charge decreases, they rise within the spectrum. The plunging nature of the $3d^2$ levels is evident in the study of levels of the Mg sequence where, towards the neutral, lowly ionized region of an isoelectronic sequence, the $3d^2$

configurations are above the ionization limit, but as the nuclear charge increased, they rapidly descended into the bound portion of the spectrum.[5] In going from a neutral atom to the negative ion of the same isoelectronic sequence, as in going from Sc to Ca$^-$, the states whose dominant components contain $3d^2$ electrons can be expected to rise rapidly. The $4s^23d$ configuration may have a similar, though less pronounced behavior. The $4s^24p$ state has been identified in Sc (well above the ground state) but not in Ti$^+$, and so isoelectronic extrapolation is not possible for predicting the binding energy of the $4p$ electron in Ca$^-$.

In this paper we first investigate the nature of the Hartree potential (no exchange) for an electron outside a Ca and Ba core, respectively, as a function of the angular momentum of the outer electron. Then we report on a study of the dynamics of configuration-interaction effects in the $s^2p\ ^2P$ states of the atoms Mg$^-$, Ca$^-$, Sr$^-$, and Ba$^-$. The latter include configurations with ns, np, and $(n-1)d$ electrons, whereas in Mg, all s, p, and d electrons have the same lowest principal quantum number, $n = 3$. We will show that this greatly diminishes the correlation contribution. Finally, we present MCHF binding energies from more extensive studies for Ca$^-$, Sr$^-$, and Ba$^-$, which have included outer correlation effects, and discuss the difficulties associated with more extensive calculations. As a check on these predictions, calculations have also been performed for the binding energy of the $4p$ electron in the $4s^24p\ ^2P$ state in Sc where experimental data are available for comparison. The present calculations predict bound states for Sr$^-$ and Ba$^-$, the extra electron being a p electron. It should be pointed out that, according to Hotop and Lineberger,[1] both Sc and Y (atoms adjacent to Ca and Sr in the Periodic Table) have stable negative ions in which the extra electron is a p electron. In La (adjacent to Ba) the extra electron is a $5d$ electron. The present MCHF studies show the $6s^26p$ state to be lower than $6s^25d$ in Ba$^-$ and with a positive electron affinity, but relativistic effects are now much greater.
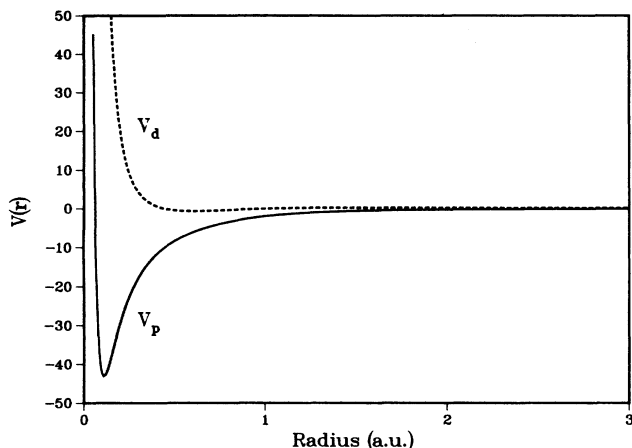
FIG. 1. The potential, $V(r) = -[20 - Y(r)]/ + l(l+1)/2r^2$, for p and d electrons outside the Ca core.
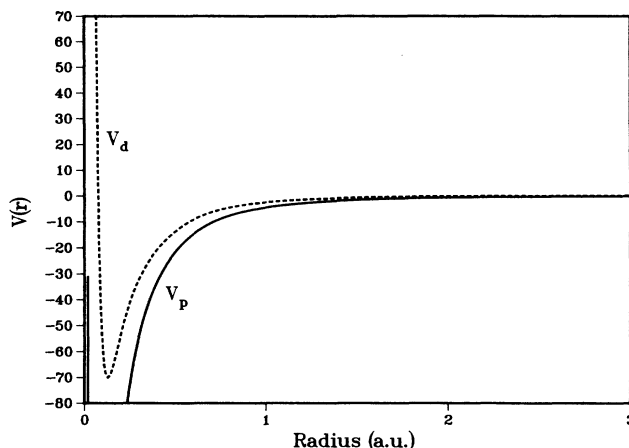

FIG. 3. The potential, $V(r) = -[56 - Y(r)]/l(l+1)/2r^2$, for p and d electrons outside the Ba core.

II. POTENTIALS FOR OUTER ELECTRONS

A comparison of the Hartree potential for an electron outside a closed ns^2 core provides a qualitative understanding of binding. Figure 1 shows the potential for both a p and d electron outside the neutral Ca core. Note that there is a distinct well for a p electron and, at best, a very shallow well for d electrons. Figure 2 is a closeup of the region near zero, that also includes the potential for an s electron. This figure clearly shows the angular momentum barrier, $l(l+1)/2r^2$, that a d electron would have to overcome. For the p electron, the barrier is small. For s electrons, there is no barrier, but the Pauli exclusion principle prevents an s electron from entering the well. In the case of the p electron, the exclusion prin-

ciple also applies, but the mean radius of the outermost $3p$ electron is only 1.27 a.u. We will see later that, when outer correlation is added, the $4s$ orbitals move out slightly, reducing the small barrier, and permitting a $4p$ electron to bind.

The situation in Ba differs somewhat. Figure 3 shows that the d well is deeper than the p well was in Ca. The closeup view in Fig. 4 shows the substantial angular momentum barrier that remains for the d electrons. There is virtually no barrier for the p and s electrons, and only the exclusion principle keeps them from entering deep into the well. The mean radii of the occupied $6s$, $5p$, and $4d$ orbitals are 5.3, 1.9, and 0.8 a.u., respectively. Thus a $6p$ electron is likely to bind, compared with Ca, but a lot of correlation would be needed to overcome the angular momentum barrier for the $5d$ electron.
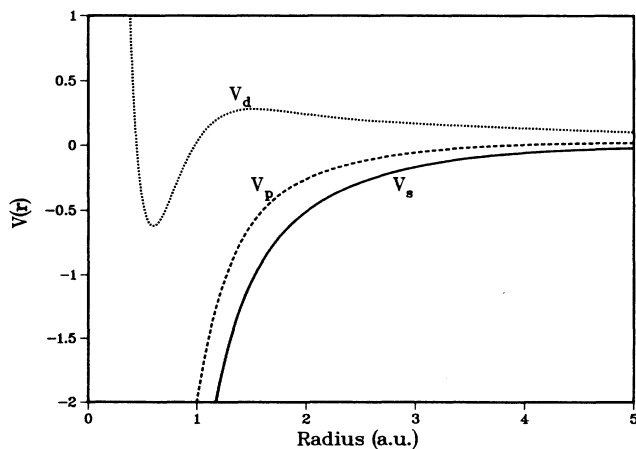

FIG. 2. The potential, $V(r) = -[20 - Y(r)]/ + l(l+1)/2r^2$, near zero for s, p, and d electrons outside the Ca core. The mean radii of the occupied $4s$ and $3p$ orbitals are 4.2 and 1.3 a.u., respectively.
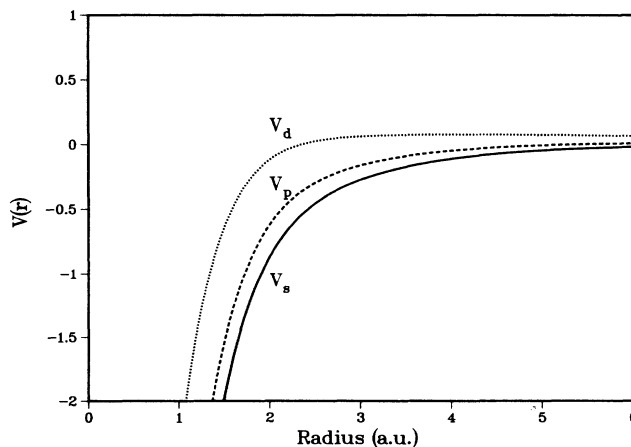

FIG. 4. The potential, $V(r) = -[56 - Y(r)]/ + l(l+1)/2r^2$, near zero for s, p, and d electrons outside the Ba core. The mean radii of the occupied $6s$, $5p$, and $4d$ orbitals are 5.3, 1.9, and 0.8 a.u., respectively.

III. LARGE CORRELATION EFFECTS
IN $s^2p\ ^2P$ STATES

States are usually classified or labeled by their dominant component in the configuration model of the atom (exceptions are highly mixed stats where no single configuration can be associated unambiguously with the state). Other configurations are present in a wavefunction expansion because of the possibility of interactions between configurations. Let $\Psi(\alpha lS)$ be an approximate total wave function for a state with label α, where

$$\Psi(\alpha LS) = \sum_i c_i \Phi(\gamma_i LS) ,\qquad\qquad (1)$$

and where $\Phi(\gamma LS)$ is a configuration state function (CSF) for the configuration γ. In a configuration-interaction calculation, the CSF's are defined in terms of a fixed basis of the radial functions for orbitals and the stationary principle leads to the secular problem,

$$\mathbf{Hc} = E\mathbf{c}$$

where $\mathbf{H} = (H_{ij})$ is the interaction matrix, and the components of the eigenvector, $\mathbf{c} = (c_i)$, are the expansion coefficients of the wave function in Eq. (1). The elements of the interaction matrix are defined as

$$H_{ij} = \langle \Phi(\gamma_i LS)|H|\Phi(\gamma_j LS)\rangle ,$$

where H is the many-electron Hamiltonian for the system. For simplicity, let $\Phi_i = \Phi(\gamma_i LS)$.

Suppose now that $\Phi_1 = \Phi(s^2p\ ^2P)$ and that the other

TABLE I. Short wave-function expansion for the $s^2p\ ^2P$ states of some negative ions showing correlation trends.

	Mg$^-$	Ca$^-$	Sr$^-$	Ba$^-$
s^2p	0.9530	0.9179	0.9073	0.8748
p^3	0.2012	0.2304	0.2283	0.2340
$sd(^1D)p$	−0.0239	−0.0449	−0.0485	−0.0595
$sd(^3D)p$	0.2119	0.2930	0.3168	0.3717
$d^2(^1S)p$	−0.0620	−0.0973	−0.1124	−0.1433
$d^2(^1D)p$	−0.0277	−0.0524	−0.0602	−0.0837

CSF's have expansion coefficients that are relatively small. Then, by perturbation theory,

$$c_i \approx H_{i1}/(H_{11} - H_{ii}) ,$$

$$\Delta E_i \approx H_{i1}^2/(H_{11} - H_{ii}) ,$$

where ΔE_i represents the lowering of the total energy by the configuration state i. Thus the strength of an interaction, in energy terms, depends on the square of an interaction matrix element divided by an energy difference. The effect may be strong if either the Coulomb interaction matrix element is large or the energy difference is small.

There are several well-known, strong interactions. One is the $s^2\ ^1S - p^2\ ^1S$ interaction which, with a spectator p electron, becomes an $s^2p\ ^2P - p^3\ ^2P$ interaction. When the principal quantum numbers of the s and p electrons are the same, this interaction is always very similar. The
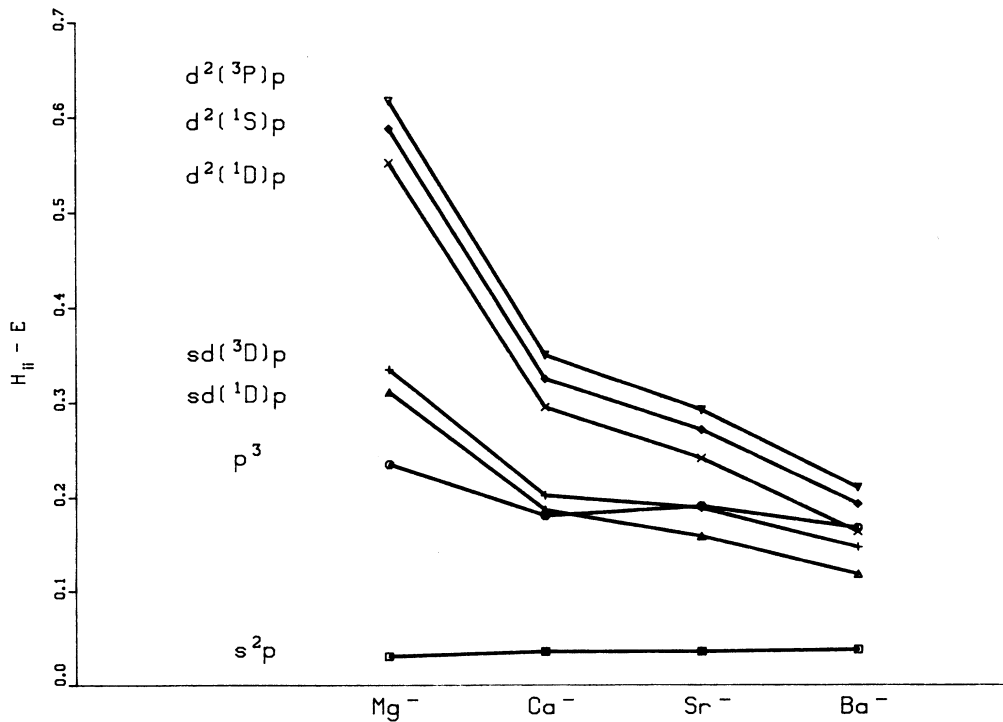

FIG. 5. Energy levels of s^2p, sdp, and d^2p configurations for the alkaline-earth elements, Mg$^-$, Ca$^-$, Sr$^-$, and Ba$^-$.
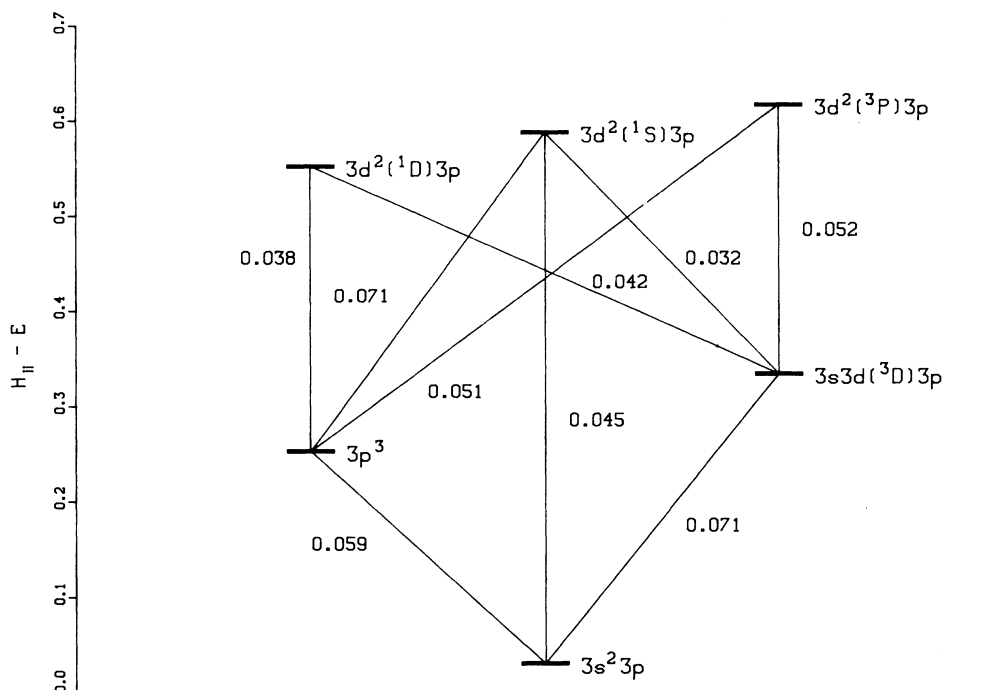
FIG. 6. Interaction diagram for s^2p, sdp, and d^2p configurations in Mg^-.
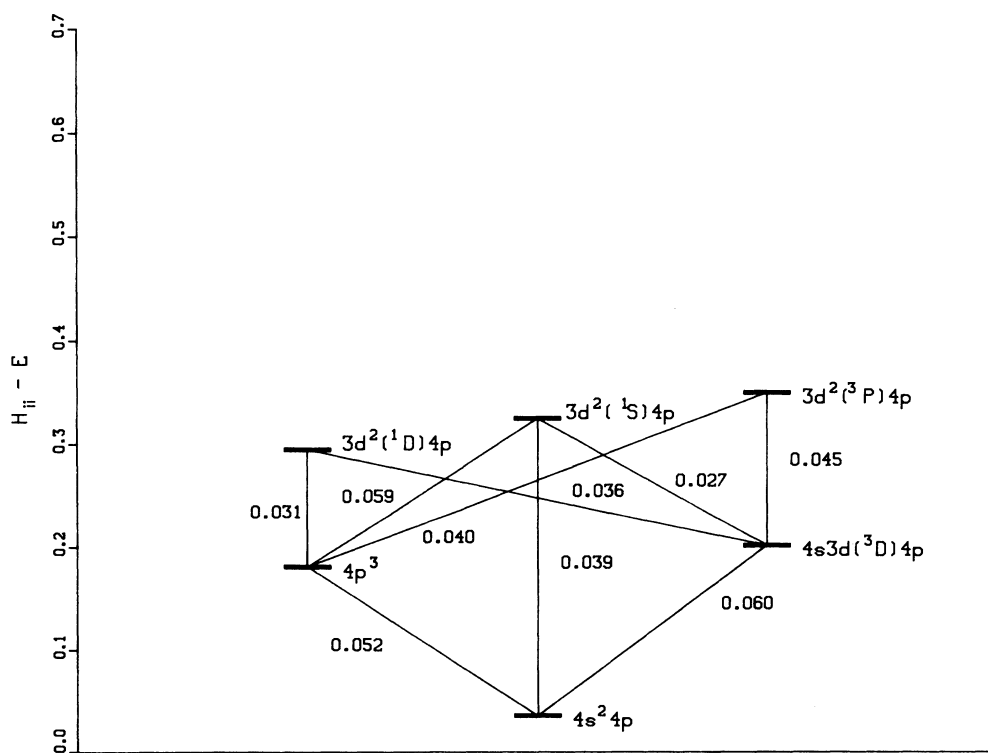

FIG. 7. Interaction diagram for s^2p, sdp, and d^2p configurations in Ca^-.

$s^2\,{}^1S-d^2\,{}^1S$ interaction is never as strong when the principal quantum numbers are the same. Another interaction is $sd\,{}^1D-p^2\,{}^1D$ [or $sd\,({}^1D)p\,{}^2P-p^3\,{}^2P$ in the present case] but now the energy difference plays a more important role. Indeed, in the aluminum isoelectronic sequence[6] where the interaction is $s^2d\,{}^2D-sp^2\,{}^2D$, the order of the diagonal energies changes as the effective nuclear charge is varied. In the atomic systems studied in this paper, the principal quantum of the d electron will be 1 less than that of the s and p electrons, except in Mg where all principle quantum numbers are the same. Finally, there are the $sp\,{}^{1,3}P-dp\,{}^{1,3}P$ interactions which usually are not as strong as s^2-p^2 interactions when the principal quantum numbers are the same, but now may be larger when the principal quantum number of the d electron is reduced, causing a smaller energy denominator. These interactions enter in the s^2p state with the s electron as the spectator electron. Similarly, the $s^2\,{}^1S-d^2\,{}^1S$ interactions also are larger because of the smaller energy denominator.

MCHF calculations were performed for $s^2p\,{}^2P$ states of Mg$^-$, Ca$^-$, Sr$^-$, and Ba$^-$ with a wave-function expansion over the configuration states

$$\{s^2p, p^3, sd\,({}^{1,3}D)p, d^2({}^1S, {}^3P, {}^1D)p\}\,{}^2P\ ,$$

where the set of s, d, p electrons for the different ions were the following:

Ion	Electrons
Mg$^-$	$3s, 3d, 3p$
Ca$^-$	$4s, 3d, 4p$
Sr$^-$	$5s, 4d, 5p$
Ba$^-$	$6s, 5d, 6p$

The mixing coefficients of this calculation are reported in Table I. Notice that the mixing of $sd\,({}^1D)p$ is small in all cases.

Table I, in effect, shows the results of all these interactions. To get a better understanding of the dynamics of the interactions between the different pairs of configuration states, the diagonal energies relative to the final total energy for the state are depicted in Fig. 5 as levels. It is clear now that p^3 and $sd\,({}^1D)p$ cross in going from Ca$^-$ to Sr$^-$ but, because of the small interaction of the latter with $s^2p\,{}^2P$, this crossing does not have a pronounced effect on correlation, other than to introduce an irregularity in the mixing coefficient for p^3, as seen in Table I. Clearly evident is the fact that the d^2p configurations have energies much closer to the lower-lying configurations in Ca$^-$, Sr$^-$, and Ba$^-$ than in Mg$^-$, particularly the $sd\,({}^3D)p$ and p^3 configurations which interact strongly and directly with $s^2p\,{}^2P$.

In Figs. 6 and 7, the important interactions are depicted graphically [$sd\,({}^1D)p$ has been omitted] for Mg$^-$ and Ca$^-$, respectively. The energy levels are represented as before, but now lines are drawn between the configuration states that interact. The strength of the interaction (or absolute value of the H_{ij}) is shown near the line. Each interaction, in a local sense, as in a 2×2 interaction matrix, reduces the energy of the lower level and raises

the energy of the higher level. In going from Mg$^-$ to Ca$^-$ the distance between the d^2p and s^2p configurations has been reduced by a factor of $\frac{1}{2}$, whereas the square of the matrix elements has been reduced by about 20–30 %. In going from Fig. 6 to Fig. 7, the d electrons change from being nd electrons to $(n-1)d$ electrons. This may explain why there is not sufficient correlation in Mg$^-$ to form a stable, negative bound state, but why there is enough correlation in Ca$^-$. At the same time, this view would predict that Zn, like Mg, does not have a stable, negative ion. Indeed, extensive calculations like those that will be reported for some heavier alkaline-earth elements, did not predict a bound state for Zn$^-$.

IV. BINDING ENERGIES FOR Ca$^-$, Sc, Sr$^-$, AND Ba$^-$

The calculations described in Sec. III can help explain the difference in the major correlation effects in Mg$^-$ compared with other alkaline-earth systems. They do not predict reliable binding energies which depend on a large number of interactions. In this section we describe a series of calculations for predicting binding energies in the systems of interest in this paper. In each case, the binding energy is the difference in energy between a (core)$s^2\,{}^1S$ state and (core)$s^2p\,{}^2P$ state. For negative ion states, this prediction requires that the diffuse part of the wave function be represented well by appropriate radial functions. These functions do not contribute a great deal to the total energy, and so, a variational procedure that includes correlation in the core at the same time, will favor the core region where there is far more correlation over the outer region, thereby providing a poor representation of the critically important, outer region. We will treat the systems as two- and three-electron systems, respectively, and in the case of Ca$^-$ ($Z=20$) and Sc ($Z=21$), compare the results with those derived from observation.

In each case, the two-electron system was computed by including all possible ^1S configurations from the set of electrons listed in Table II as calculation (a), using the MCHF method.[7] In this calculation all radial functions were varied, including those of the core. In calculations (b) and (c), additional electrons were allowed to define the set of configuration states. A generalized Brillouin's theorem was applied to eliminate configuration states obtained through single substitution of electrons from large components in order to produce the "reduced" form for a ^1S wave function.[8] In the latter calculations, all but the core orbitals were varied. The calculations for the $s^2p\,{}^2P$ states were similar, but varied somewhat with each system.

A. Calculations for Ca$^-$

In the calculations for Ca$^-$, all possible three-electron configuration states were generated from the electrons of calculation (a) and all orbitals (including the core orbitals) were varied. In calculation (b), the set of electrons defining the configuration states was extended. If all the possible configuration states resulting from this set of

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TABLE II. Total energies and predicted binding energies (ΔE) for a series of calculations.

	Ca	Ca$^-$	ΔE
(a) $4s, 4p, 3d$	-676.78609	-676.77648	-0.261
(b) $+5s, 5p, 4d, 4f$	-676.78705	-676.78860	0.042
(c) $+6s, 6p, 5d, 5f, 5g$	-676.78711	-676.78967	0.070
(d) with relativistic shift	-679.56673	-679.56899	0.062
Observed (Ref. 3)			0.043 ± 0.007

	Sc$^+$	Sc	ΔE
(a) $4s, 4p, 3d, 4f$	-759.49629	-759.69097	5.297
(b) $+5s, 5p, 4d$	-759.49704	-759.69888	5.492
(c) $+6s, 6p, 5d, 5f, 5g$	-759.49718	-759.70194	5.571
(d) with relativistic shift	-762.93897	-763.14200	5.524
Observed (Ref. 11)			5.685

	Sr	Sr$^-$	ΔE
(a) $5s, 5p, 4d$	-3131.57128	-3131.56611	-0.141
(b) $+6s, 6p, 5d, 4f$	-3131.57210	-3131.57539	0.089
(c) $+7s, 7p, 6d, 5f, 5g$	-3131.57216	-3131.57686	0.128
(d) with relativistic shift	-3175.25652	-3175.26041	0.106

	Ba	Ba$^-$	ΔE
(a) $6s, 6p, 5d, 4f$	-7883.56830	-7883.57285	0.124
(b) $+6s, 6p, 5d, 5f$	-7883.56887	-7883.57842	0.260
(c) $+7s, 7p, 6d, 6f$	-7883.56891	-7833.57909	0.277
(d) with relativistic shift	-8111.70570	-8111.71113	0.148

electrons were included in the MCHF wave-function expansion, the radial functions would not be uniquely defined. In calculations for neutral atoms, a generalized Brillouin's theorem would normally be applied to the dominant component, $4s^2 4p$, so that the $4p$ energy parameter would be close to the binding energy (Koopmanns's theorem for a MCHF wave-function expansion), but because the $4p$ radial function is to be bound even when the energy for Ca$^-$ may still be above that of the Ca ground state, Brillouin's theorem was applied to the $4s\,3d\,(^3D)4p$ component. As a result, the singly substituted state $4s^2 5p$, for example, was allowed to remain, but the configuration state $4s\,3d\,(^3D)5p$ was removed. The same process was applied to the $4s \rightarrow 5s$ replacement and the $3d \rightarrow 4d$ replacement. With this procedure, the MCHF calculations were then sufficiently stable to allow for the variation of all the orbitals outside the core. Notice that this energy is already nearly as low as the longer wave-function expansion described previously[4] where only new orbitals were varied.

Finally, in calculation (c), the set of electrons defining the configuration states was extended further, but not all configuration states were retained. Among those omitted were the high-angular states such as

$$4f\,5g^2, \quad 5f\,5g^2, \quad 6p\,5p^2, \quad 5d\,5f\,5g, \quad 6s\,5f\,5g\ ,$$

$$5s\,5f\,5g, \quad 5d\,4f\,5g, \quad 4d\,4f\,5g, \quad 6s\,4f\,5g\ .$$

The remaining new configuration states were added to the results of calculation (b) after configuration states

with coefficients less than 0.0002 had been omitted. This reduced the length of the wave-function expansion for calculation (b) from 130 configuration states to 116, but raised the energy by only 1.1×10^{-7} a.u. Brillouin's theorem was applied and all outer orbitals varied.

B. Calculations for Sc

Calculations were performed for this case because it is in the same isoelectronic sequence as Ca$^-$ and a binding energy is available from observation for comparison purposes.

Neutral Sc is interesting because the Hartree-Fock energies of $4s^2 4p\ ^2P$ and $4s\,3d\,(^3D)4p\ ^2P$ are as close to being degenerate as any ever computed, namely, $-759.631\,682$ and $-759.631\,866$, respectively. Correlation is greater for the former than the latter and, once it has been represented in the wave-function expansion, the lower energy is predominantly $4s^2 4p$. Because of this degeneracy, the calculation for Sc could not proceed exactly as that for Ca$^-$: even in calculation (a), the configurations containing $4f$ electrons were needed to break the degeneracy. As more electrons were included, Brillouin's theorem was applied to the $4s^2 4p$ component when deleting singly substituted configurations arising from $4s \rightarrow ns$ replacements [such as $4s\,5s\,(^1S)4p$] and $4p \rightarrow np$, and $4s\,3d\,(^3D)4p$ when deleting configuration states arising from $3d \rightarrow nd$ single replacements.

TABLE III. The eight largest configuration states in the wave-function expansions of calculation (c).

Ca⁻		Sc		Sr⁻		Ba⁻	
0.7856	$4s^24p$	0.8220	$4s^24p$	0.8259	$5s^25p$	0.8526	$6s^26p$
0.4873	$4s^25p$	0.4498	$4s3d(^3D)4p$	0.3987	$5s^26p$	0.3328	$6s5d(^3D)6p$
0.2251	$4s3d(^3D)4p$	−0.1802	$4s3d(^1D)4p$	0.2530	$5s4d(^3D)5p$	−0.2217	$6s^27p$
0.1875	$4p^3$	0.1764	$4p^3$	0.1973	$5p^3$	0.2150	$6p^3$
0.1385	$4p^2(^1S)5p$	−0.1475	$3d^2(^1S)4p$	0.1178	$5s6s(^1S)6p$	−0.1210	$5d^2(^1S)6p$
−0.1315	$4s5s(^1S)5p$	−0.0959	$3d^2(^3P)4p$	−0.1141	$5p^2(^1S)6p$	−0.0939	$5d^2(^3P)6p$
−0.0632	$3d^2(^1S)4p$	−0.0744	$3d^2(^1D)4p$	−0.0794	$4d^2(^1S)5p$	−0.0923	$6s7s(^1S)7p$
−0.0513	$3d^2(^3P)4p$	0.0773	$4s4d(^1D)4p$	−0.0616	$4d^2(^3P)5p$	−0.0695	$6p^2(^1S)7p$

C. Calculations for Sr⁻

These calculations followed those described for Ca⁻, except that now the principal quantum number of s, p, and d orbitals have increased by 1.

D. Calculations for Ba⁻

These calculations were similar to the ones for Sr⁻, with principal quantum numbers increased by 1, but the $5g$ orbital was replaced by a $6f$ orbital. Stability problems were encountered with the $5g$ orbital, partly because its contribution to the correlation was negligible: the contribution from $6f$, though small, was somewhat larger.

V. DISCUSSION AND RESULTS

The results of all these calculations are presented in Table II. Also included are the energies obtained by including the relativistic shift corrections (mass-velocity, spin-spin contact, and Darwin terms[9]) in the energy calculation for each two- and three-electron system. For both Sr and Ba, the configurations deleted through the application of Brillouin's theorem were now included in the expansion since they could affect the relativistic shift correction. These $nsn's$ "cross terms" were particularly important for the relativistic shift correction of the Ba ns^2 ^1S state. For each calculation, the predicted binding energy of the p electron is tabulated computed from the difference of the two energies. In the case of Ca⁻ and Sc, the final results are compared with experiment.

Notice that calculation (a) underestimates the binding energy. Indeed, for Ca and Sr, the binding energy is still negative. Calculation (b) is a significant improvement, though for Ca⁻ and Sr⁻, calculation (c) is still important. The relativistic shift effect is greater in the two-electron system than the three-electron system and therefore reduces the binding energy by about 0.008 eV in Ca⁻, by 0.022 eV in Sr⁻, and by 0.129 eV for Ba⁻, increasing as expected for heavier systems.

Experimental observations are available only for Ca⁻ and Sc. In the case of Ca⁻, the binding energy predicted by the present calculation is too large, whereas for Sc it is too small. Perturbation theory[10] can yield the correction to the binding energy as a second-order correction to the energy difference. The situation is a little more complex than the alkali-metal elements where the theory is well established and where the core of the atom and the ion is

essentially the same. The most important correlation effect omitted in the present study is the correlation between $(n-1)p^6$ and the outer electrons, a core-polarization effect. In the ^2P states, there is both a core-polarization correction for ns^2 and for np. Thus, in Sc, where the $4s$ orbitals of both systems are essentially the same, the core-polarization correction from the $4s^2$ shell would cancel, leaving the correction from the $4p$ electron. The present study has underestimated the binding energy of the $4p$ electron by omitting this effect. In the other systems as well, there are similar core-polarization corrections. Table III lists the eight largest components of the wave function of calculation (c) of Table II and shows that the np orbital plays an important role in the representation of the wave function. Its mean radius is only between 8% and 13% larger than that of ns. Though the core polarization is less for p electrons than for s electrons, as in Sc, this neglected effect would increase the binding energy. But there is an important difference, namely, the relaxation of the ns orbital. In each case this radius has increased by about 15%. Thus there would be more correlation between the core and the ns^2 subshell of the neutral atom than the negative ion, and this would tend to reduce the binding energy of the negative ion electron. This is consistent with the present result for Ca⁻ which overestimates the experimental binding energy.

Relativistic effects have been estimated in this calculation and, as mentioned earlier, in Ba the cross terms, which could be omitted in the nonrelativistic calculation because of the variational nature of the orbital calculation, were included in the wave-function expansion for the estimation of the relativistic shift. These terms were more important in the calculation of the neutral atom than the negative ion and reduced the electron affinity of Ba by almost 0.1 eV. On the other hand, studies of core polarization[12] for the simpler $nsnp$ ^3P state of Cs⁻ showed that the relativistic correction to the binding energy decreased as core polarization was added. Because of the importance of the relativistic effect, the results for Ba have the greatest uncertainty associated with them.

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