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Valence-core electron exchange interaction and the collapse of 4*f* and 5*d* orbitals in the cesium isoelectronic sequence

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As one progresses along the isoelectronic sequence of Cs, the ground state changes from $6s_{1/2}$ (Cs, Ba$^+$) to $5d_{3/2}$ (La^{2+}) to $4f_{5/2}$ (Ce^{3+}, Pr^{4+}). The relativistic Hartree-Fock and model-potential calculations reported here are aimed at obtaining a better understanding of variations in the ordering of the states as the ion charge increases. The 5*d* and 4*f* orbitals are found to "collapse" as the increasing Coulomb and exchange attractions overcome centrifugal repulsion. Valence-core electron exchange is found to be crucial for the proper ordering of the states as well as for reliable fine-structure splittings. Furthermore, the collapse of the 5*d* and 4*f* orbitals greatly enhances the sensitivity of the properties of these states to small perturbations, so that even details of the exchange interaction, including nonlocal effects, as well as core-relaxation and -polarization effects, are required in order to compute accurate ionization potentials and fine-structure splittings.

I. INTRODUCTION

In a recent paper,[1] we studied the relative importance of relativistic effects, core polarization and relaxation in ionization potentials for Cs through Pr^{4+}. It was found that both relativistic and core-polarization effects have an essential influence on the ionization potentials of *s*, *d*, and *f* states, whereas core relaxation is important for the *f* and *d* states only. It was also shown that by including relativistic effects, core polarization and relaxation in the single-configuration Hartree-Fock ionization potentials, it is possible to achieve an average agreement with experiment of around 1 to 2%. The present paper is devoted to further studies of ionization potentials of *s*, *d*, and *f* states and their behavior along the cesium isoelectronic sequence. As is well established experimentally,[2,3] the $6s_{1/2}$ state is the ground state only for the first two systems of the cesium isoelectronic sequence, whereas for the remaining systems first the $5d_{3/2}$ and then the $4f_{5/2}$ states take that role. We demonstrate in this paper that the inclusion of valence-core electron exchange in the energy operator used to compute the wave functions is crucial for the proper ordering of the theoretically determined states of the systems and, in consequence, for computations of the correct ionization potentials, and that this effect is strongly linked to the gradual collapse of the 5*d* and 4*f* orbitals. The behavior of the inner and outer wells of the effective potential along the cesium isoelectronic sequence as well as the way this behavior is affected by including the local valence-core electron exchange interaction in the effective potential is studied using the model-potential approach with no free parameters. The influence of the accuracy of the representation employed for valence-core electron exchange as well as of the nonlocal effects in exchange on the computed ionization potentials is investigated by means of fully relativistic Hartree-Fock (RHF) calculations.

II. CALCULATIONS

To investigate qualitatively the changes in the effective potentials along the cesium isoelectronic sequence as well as the influence of valence-core electron exchange, the relativistic model-potential (RMP) approach discussed in detail in our previous papers[4,5] was employed. Two versions of this approach were used. In the first (RMP) the valence electron was affected by the field of the core $V(r)$ which included only the nuclear attraction and Coulomb interelectronic repulsion,

$$V(r)=-\frac{Z}{r}+\frac{1}{r}\int_0^r \rho_c(r')dr'+\int_r^\infty \frac{\rho_c(r')}{r'}dr' , \qquad (1)$$

where $\rho_c(r')$ is the radial electron density of the core and Z is the charge on the nucleus (atomic units are used throughout this paper).

In the second version (RMP + SCE) the local valence-core electron exchange interaction approximated by the "semiclassical exchange" (SCE) potential V_{SCE}, suggested independently by Furness and McCarthy[6] and by Riley and Truhlar,[7] was added to the core potential $V(r)$ of Eq. (1). Here,

$$V_{\mathrm{SCE}}(r)=\tfrac{1}{2}[E-V(r)]-\tfrac{1}{2}\{[E-V(r)]^2+\beta^2\}^{1/2} , \qquad (2)$$

where $E<0$ is the valence electron energy, $V(r)$ is the core potential of Eq. (1), and for cores with doubly occupied spatial orbitals,

$$\beta^2=\rho_c(r)/r^2 . \qquad (3)$$

For bound states ($E<0$) as r approaches the classical turning point r_c, V_{SCE} becomes equal to $-\frac{1}{2}\beta$, whereas for $r \gg r_c$ it increases in magnitude and tends to E. Therefore the potential of Eq. (2) must be cut shortly before the classical turning point and replaced by its form at the classical turning point, namely, $-\frac{1}{2}\beta$, which tends to zero for large r.

The SCE approximation does not depend on any empirical or adjustable parameter and has turned out to be very successful. As previously found in our test calculations[5] for Rb and Ag, it yields one-electron energies in agreement with those obtained including the accurate, nonlocal exchange interaction with an rms error of below 4%.

To determine the influence of the nonlocal effects in the valence-core electron exchange on the ionization potentials, single-configuration relativistic Hartree-Fock calculations, labeled as RHF(FC), were performed in the "frozen-core" approximation using the parent ion of a system as a core. Finally, for the sake of comparison, the "relaxed-core" single-configuration relativistic Hartree-Fock calculations of ionization potentials, labeled as RHF(RC), were performed without and with the core-polarization effect (CP) included through the core-polarization model potential,[8] V_{pol}, added to the one-electron Hamiltonian of the valence electron,[9]

$$V_{\mathrm{pol}}(r)=-\tfrac{1}{2}\alpha r^2(r^2+r_0^2)^{-3}\ , \tag{4}$$

where α is the static dipole polarizability of the core (the polarizabilities calculated for parent ions by Fraga *et al.*[10] were used here) and r_0 is the cutoff radius of the core taken as the mean radius $\langle r\rangle$ of the outermost orbital of the core. The values of α and r_0 parameters used here were the same as employed in our previous study.[1]

III. DISCUSSION OF RESULTS

A. Orbital collapse and valence-core exchange

As the charge of the ion core increases from $z=1$, one expects the ordering of levels to change from the typical atomic sequence, in which the value of $n+l$ plays the dominant role,[11] to one characteristic of hydrogenic ions, in which the value of n is of primary importance. Thus along the Cs isoelectronic sequence the ordering changes from $6s<6p,5d,4f$ (Cs, Ba$^+$) to $4f<5d<6s,6p$ (Ce^{3+}, Pr^{4+}) as z increases from 1 to 5.

The phenomenon of orbital "collapse" has been described by Cheng and Froese Fischer[12] and references therein. It refers to an almost discontinuous drop in the energy and size of usually a d or f orbital in response to changes in the effective potential

$$V_{\mathrm{eff}}(r)=V(r)+l(l+1)/(2r^2)\ , \tag{5}$$

as the atomic number Z is increased. For sufficiently heavy neutral atoms, $V_{\mathrm{eff}}(r)$ has two wells separated by a barrier. As one moves along the periodic table of atoms to higher Z, the narrow inner well deepens and widens and the barrier drops somewhat.[12] If the barrier is sufficiently opaque,

$$\int_{r_1}^{r_2} dr[2V_{\mathrm{eff}}(r)-2E]^{1/2}\gg 1\ , \tag{6}$$

at the orbital energy E (r_1 and r_2 are the classical turning points on either side of the barrier), then the two wells are fairly isolated and the inner well has little effect until it becomes deep and wide enough to support a state below the eigenenergy E of the isolated outer well. In the JWKB approximation,[13] this condition can be written

$$\int_{r_0}^{r_1} dr[2E-2V_{\mathrm{eff}}(r)]^{1/2}>\pi/2\ , \tag{7}$$

where r_0 and r_1 are the classical turning points of the inner well. The left-hand side of Eq. (7) varies essentially as the width of the well times the square root of the well depth below E. When this condition is satisfied, even in the presence of an opaque barrier, the orbital collapses from the outer well to the lower eigenstate of the inner well.

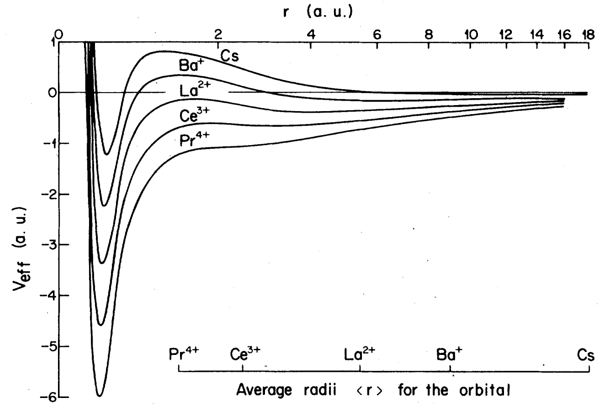

FIG. 1. The effective potential curves for the $4f_{5/2}$ states in Cs through Pr^{4+} obtained using the relativistic model-potential approach with valence-core electron exchange neglected (RMP). The mean radii $\langle r\rangle$ of the $4f_{5/2}$ orbitals obtained with these effective potentials are also marked. The horizontal scale is proportional to the logarithm of $r+2$ a.u.

If, instead of considering atoms along the periodic table, one moves along an isoelectronic sequence, the increasing charge z on the ion core causes the inner well and barrier to drop more rapidly and also deepens the outer well. The result, as shown by Cheng and Froese Fischer[12] in Hartree-Slater calculations of the Xe isoelectronic sequence, is an orbital collapse which begins earlier and proceeds more gradually.

Our RMP calculations of $V_{\mathrm{eff}}(r)$ for $4f_{5/2}$ orbitals in the Cs isoelectronic sequence Cs to Pr^{4+} are shown in Figs. 1 and 2. The effective potentials in Fig. 1 do not include exchange effects in $V(r)$ and are identical to those

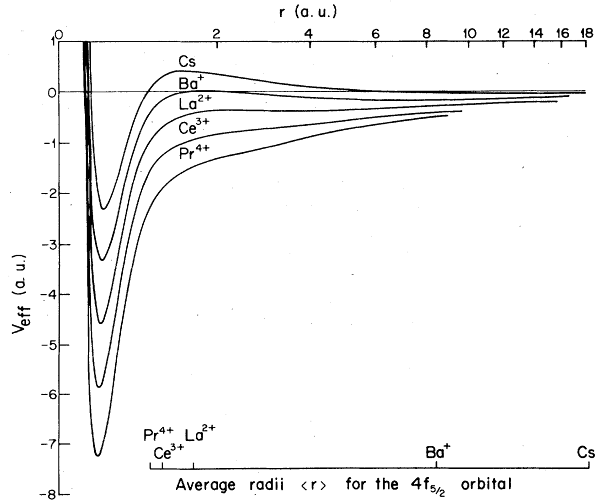

FIG. 2. The effective potential curves for the $4f_{5/2}$ states in Cs through Pr^{4+} obtained using the relativistic model-potential approach with valence-core electron exchange represented by the semiclassical exchange scheme (RMP + SCE). The mean radii $\langle r\rangle$ of the $4f_{5/2}$ orbitals obtained with these effective potentials are also marked. The horizontal scale is as in Fig. 1.

for the $4f_{7/2}$ orbitals. In Fig. 2, exchange is included in the semiclassical exchange (SCE) approximation,[6,7] and consequently $V_{\text{eff}}(r)$ for the $4f_{7/2}$ orbital differs only by the dependence of the local exchange term on the one-electron energy. The lowering of both outer and inner wells and also of the potential barrier as Z is increased can be seen clearly in the figures as well as in Table I. The resulting orbital contraction can be followed in the average orbital radii $\langle r \rangle$ which are indicated at the bottom of both figures.

From a comparison of Figs. 1 and 2 as well as from Table I, one can see the effect of core-valence exchange on the shape of the effective potentials of the $4f_{5/2}$ states. The exchange interaction considerably enlarges the size of the inner well by an amount which increases slowly along the sequence, whereas the outer well is hardly affected. The influence of exchange is also seen clearly in the height of the centrifugal barrier, which is lowered strongly and even disappears for the Ce^{3+} system when exchange is included in the potential. (A similar effect of exchange on the formation of the collapsed $4f$ state was predicted by Band *et al.*[14] for neutral "Dirac-Fock atoms" lanthanum and europium.) The barrier height is important because if the barrier is absent or low (fairly "transparent"), then even an inner well which is not large enough to support an isolated bound state below E, as, for example, one associated with a low barrier and for which condition (7) is not satisfied, can cause a significant contraction or "partial collapse" of the orbital. This situation seems to describe the $4f$ orbitals in Ce^{3+} and to a lesser degree in La^{2+} when valence-core exchange is omitted (Fig. 1), and a beginning of partial collapse also seems indicated in Ba^{+} when exchange is included (Fig. 2).

The effective potentials of the $5d_{3/2,5/2}$ orbitals have deeper wells than those of the $4f_{5/2,7/2}$ states, but have a similar dependence on Z. We can see from Table I that the inner well for the $5d_{3/2,5/2}$ states, which is already 15 to 50 times deeper than the inner well for $4f_{5/2,7/2}$ states [because of the smaller angular momentum and, in consequence, smaller centrifugal repulsive potential in Eq. (5)] also increases along the sequence. The outer well, however, is distinct for the $5d_{3/2,5/2}$ states only in neutral cesium and disappears completely in singly ionized barium.

The influence of exchange on the shape of the effective potential curve can be seen directly in Figs. 3 and 4, where the potential curves with and without exchange are compared for the $4f_{5/2}$ state in Ce^{3+} and for the $5d_{3/2}$ state in Cs, respectively. These two figures display how the exchange effects assist the collapse of the $4f$ or $5d$ orbitals. The influence on the shape of the eigenfunction of the valence electron is demonstrated by calculating the relative orbital contraction due to exchange,

$$(\langle r \rangle_{\text{RMP}} - \langle r \rangle_{\text{RMP+SCE}}) / \langle r \rangle_{\text{RMP}}$$

or

$$(\langle r \rangle_{\text{RMP}} - \langle r \rangle_{\text{RHF(FC)}}) / \langle r \rangle_{\text{RMP}} ,$$

which is shown in the last two columns of Table II for the valence-core electron exchange represented both by the approximate local term of Eq. (2) in the RMP + SCE approach and by the accurate nonlocal operators in the RMF(FC) calculations. Differences between the results of these two approaches does not exceed 6%. It can be seen

TABLE I. The depth of the inner well (D_{inn}), outer well (d_{out}), and the height of centrifugal barrier (H_{barr}), computed in the model-potential without (RMP) and with semiclassical exchange term (RMP + SCE), as well as the resulting increase in the depth of inner well (ΔD_{inn}) and outer well (Δd_{out}), and the decrease in the height of centrifugal barrier (ΔH_{barr}) due to exchange contribution. (The "—" entry means that the outer well and the centrifugal barrier are missing.)

System		D_{inn}			d_{out}			H_{barr}		
and	state	RMP	RMP + SCE	ΔD_{inn}	RMP	RMP + SCE	Δd_{out}	RMP	RMP + SCE	ΔH_{barr}
Cs	$5d_{3/2}$	1755.513	1868.718	113.205	2.268	2.276	0.0083	1.4877	0.0719	1.4242
	$5d_{5/2}$	1755.513	1868.718	113.205	2.268	2.276	0.0083	1.4877	0.0723	1.4237
Ba^{+}	$5d_{3/2}$	1872.840	1988.844	116.004						
	$5d_{5/2}$	1872.840	1988.843	116.003						
La^{2+}	$5d_{3/2}$	1994.522	2114.100	119.578						
	$5d_{5/2}$	1994.522	2114.097	119.575						
Ce^{3+}	$5d_{3/2}$	2122.023	2243.335	121.312						
	$5d_{5/2}$	2122.023	2243.330	121.307						
Pr^{4+}	$5d_{3/2}$	2253.275	2377.257	123.982						
	$5d_{5/2}$	2253.275	2377.250	123.975						
Cs	$4f_{5/2}$	33.763	63.224	29.461	1.134	1.134	0.0	22.980	12.642	10.338
	$4f_{7/2}$	33.763	63.224	29.461	1.134	1.134	0.0	22.980	12.642	10.338
Ba^{+}	$4f_{5/2}$	61.660	92.332	30.672	4.534	4.535	0.0006	13.445	5.095	8.351
	$4f_{7/2}$	61.660	92.332	30.672	4.534	4.535	0.0006	13.445	5.095	8.351
La^{2+}	$4f_{5/2}$	92.467	124.538	32.071	10.208	10.296	0.0880	6.459	0.434	6.113
	$4f_{7/2}$	92.467	124.533	32.066	10.208	10.294	0.0856	6.459	0.448	6.097
Ce^{3+}	$4f_{5/2}$	125.892	159.687	33.795	18.252			1.552		
	$4f_{7/2}$	125.892	159.679	33.787	18.252			1.552		
Pr^{4+}	$4f_{5/2}$	162.082	197.393	35.311						
	$4f_{7/2}$	162.082	197.393	35.311						

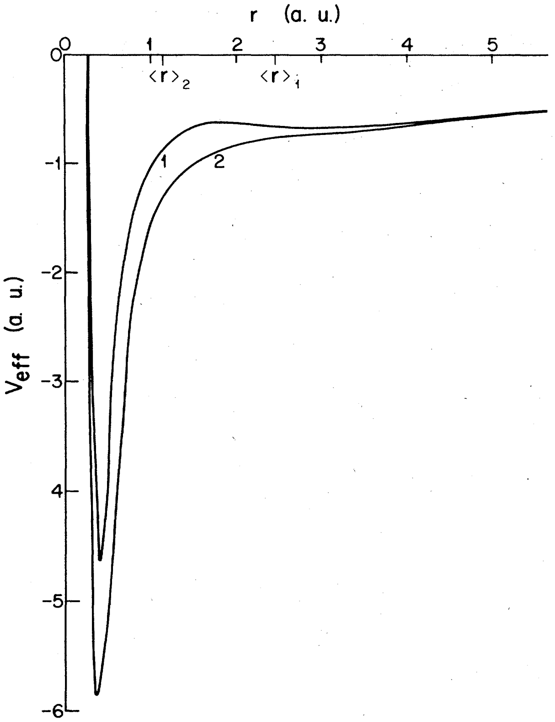

FIG. 3. Comparison of the effective potential curves obtained for the $4f_{5/2}$ state in Ce^{3+} using the model-potential approach without (1) and with (2) the valence-core electron exchange included.

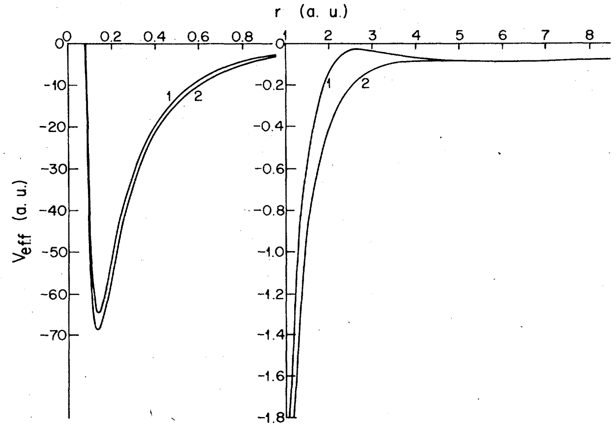

FIG. 4. Comparison of the effective potential curves obtained for the $5d_{3/2}$ state in Cs using the model-potential approach without (1) and with (2) the valence-core electron exchange included.

from the data of Table II that the relative orbital contraction due to exchange decreases steadily along the sequence for the $6s_{1/2}$ states, whereas for the $5d_{3/2,5/2}$ and $4f_{5/2,7/2}$ states it reaches a maximum for the systems undergoing collapse and then slowly decreases for more highly ionized members of the sequence. Consequently, the exchange interaction, by increasing the inner-well size while leaving the outer well largely unchanged, makes the collapse of the $5d$ and $4f$ orbitals more sudden. This ef-

TABLE II. The absolute and relative contribution of exchange to ionization potentials along cesium isoelectronic sequence as well as the relative contraction of orbitals due to exchange as evaluated in the RMP + SCE and RHF(FC) approaches.

System and state		$IP_X - IP_{RMP}$ (eV)		$100(IP_X - IP_{RMP})/IP_X$		$100(\langle r\rangle_{RMP} - \langle r\rangle_x)/\langle r\rangle_{RMP}$	
		X = RMP + SCE	X = RHF(FC)	X = RMP + SCE	X = RHF(FC)	X = RMP + SCE	X = RHF(FC)
Cs	$6s_{1/2}$	0.573	0.595	16.6	17.2	16.25	16.45
Ba^+	$6s_{1/2}$	1.098	1.244	11.9	13.3	11.34	12.20
La^{2+}	$6s_{1/2}$	1.542	1.821	9.42	10.9	8.78	9.74
Ce^{3+}	$6s_{1/2}$	1.938	2.349	7.82	9.32	7.19	8.11
Pr^{4+}	$6s_{1/2}$	2.301	2.844	6.71	8.16	6.11	7.00
Cs	$5d_{3/2}$	0.173	0.226	10.2	12.9	19.18	23.98
	$5d_{5/2}$	0.164	0.230	9.71	13.1	18.37	24.18
Ba^+	$5d_{3/2}$	1.634	2.262	20.9	26.8	27.59	32.90
	$5d_{5/2}$	1.563	2.232	20.3	26.6	26.96	32.60
La^{2+}	$5d_{3/2}$	3.248	4.371	19.3	24.3	21.18	25.23
	$5d_{5/2}$	3.132	4.310	18.8	24.2	20.93	25.08
Ce^{3+}	$5d_{3/2}$	4.650	6.165	16.7	21.0	16.39	19.81
	$5d_{5/2}$	4.503	6.086	16.7	20.9	16.32	19.74
Pr^{4+}	$5d_{3/2}$	5.887	7.737	14.5	18.3	13.19	16.15
	$5d_{5/2}$	5.714	7.644	14.3	18.2	13.16	16.14
Cs	$4f_{5/2}$	0.001	0.001	0.12	0.12	0.26	0.14
	$4f_{7/2}$	0.001	0.001	0.12	0.12	0.19	0.10
Ba^+	$4f_{5/2}$	0.078	0.077	2.23	2.20	6.21	6.32
	$4f_{7/2}$	0.076	0.078	2.17	2.23	6.10	6.39
La^{2+}	$4f_{5/2}$	5.186	6.216	39.5	43.9	70.64	73.14
	$4f_{7/2}$	5.007	6.082	38.6	43.3	70.14	72.79
Ce^{3+}	$4f_{5/2}$	14.417	15.758	46.4	48.6	53.83	55.82
	$4f_{7/2}$	14.172	15.579	46.1	48.5	54.00	56.01
Pr^{4+}	$4f_{5/2}$	19.682	21.118	37.8	39.5	28.87	31.35
	$4f_{7/2}$	19.452	20.996	37.7	39.4	29.09	31.61

fect is seen clearly in the $\langle r \rangle$ values of the $4f_{5/2}$ states shown at the bottom of Figs. 1 and 2.

B. Ionization potentials and ordering of energy levels

In Table III we present the ionization potentials calculated by using the relativistic model-potential approach without (RMP) and with valence-core electron exchange (RMP + SCE), as well as by employing the relativistic single-configuration Hartree-Fock method in the "frozen parent-ionlike core" approximation [RHF(FC)]. The last two approaches differ only in the way the exchange is represented. For the sake of comparison, the results obtained with the relaxed-core relativistic Hartree-Fock method without [RHF(RC)] and with core-polarization effects [RHF(RC) + CP] are also given. It can be seen from this table as well as from Fig. 5, where the orderings of energy levels obtained from the different theoretical approaches are presented and compared with experimental results, that neglecting exchange effects in the effective potential leads to the wrong ordering of energy levels in the model-potential approach for La^{2+}, Ce^{3+}, and Pr^{4+} and, in consequence, to the wrong designation of the ground state for these systems. Including even an approximate local representation of the valence-core electron exchange in the effective potential leads to the correct prediction of the ground state of each system and yields the correct ordering of energy levels except for La^{2+}, where the proper position of the $4f$ levels (i.e., below that of $6s_{1/2}$ level) is obtained only when accurate nonlocal exchange, core-relaxation and -polarization contributions are included. Including exchange also greatly improves the agreement of theoretical and experimental term splittings (cf. Fig. 5). Further improvements of the term splittings are observed as accurate nonlocal exchange, core relaxation and finally core polarization are added in the RHF(FC), RHF(RC), and RHF(RC) + CP calculations, respectively. The accuracy and nonlocal effects in exchange are much more important for the positions (or ionization potentials) of the collapsing $5d_{3/2,5/2}$ and $4f_{5/2,7/2}$ levels than for the relatively stable $6s_{1/2}$ levels, for which the local semiclassical exchange approximation seems sufficiently accurate. The relaxation of the core is particularly important for the $4f_{5/2,7/2}$ states, whereas core polarization is important for the states of all three symmetries.

Table II shows the absolute and relative contributions of the valence-core electron exchange to ionization potentials evaluated in the RMP + SCE and RHF(FC) approaches. It can be seen from this table that the absolute contribution of exchange to ionization potentials of the $6s_{1/2}$ states increases steadily along the sequence, whereas its relative share in the ionization potential decreases considerably. A similar increasing trend in the absolute contribution of exchange is observed for the $5d_{3/2,5/2}$ and $4f_{5/2,7/2}$ states, whereas the relative contribution reaches

TABLE III. The ionization potentials for the $6s_{1/2}$, $5d_{3/2,5/2}$, and $4f_{5/2,7/2}$ states in the cesium isoelectronic sequence computed with different methods and compared with experimental data of Refs. 2 and 3. For the description of theoretical methods see text.

System		Ionization potentials (eV)					
and state		RMP	RMP + SCE	RHF(FC)	RHF(RC)	RHF(RC) + CP	Experiment
Cs	$6s_{1/2}$	2.870	3.443	3.465	3.483	3.801	3.893
Ba^+	$6s_{1/2}$	8.094	9.192	9.338	9.366	9.793	10.001
La^{2+}	$6s_{1/2}$	14.833	16.375	16.654	16.693	17.178	17.487
Ce^{3+}	$6s_{1/2}$	22.843	24.781	25.192	25.237	25.760	26.013
Pr^{4+}	$6s_{1/2}$	32.002	34.303	34.846	34.899	35.446	35.329
Cs	$5d_{3/2}$	1.526	1.699	1.752	1.761	2.121	2.096
	$5d_{5/2}$	1.525	1.689	1.755	1.764	2.119	2.084
Ba^+	$5d_{3/2}$	6.184	7.818	8.446	8.586	9.465	9.397
	$5d_{5/2}$	6.155	7.718	8.387	8.520	9.380	9.298
La^{2+}	$5d_{3/2}$	13.599	16.847	17.970	18.193	19.191	19.171
	$5d_{5/2}$	13.503	16.635	17.813	18.021	18.994	18.973
Ce^{3+}	$5d_{3/2}$	23.185	27.835	29.350	29.615	30.665	30.582
	$5d_{5/2}$	22.997	27.500	29.083	29.334	30.367	30.274
Pr^{4+}	$5d_{3/2}$	34.588	40.475	42.325	42.619	43.690	43.253
	$5d_{5/2}$	34.290	40.004	41.934	42.213	43.268	42.823
Cs	$4f_{5/2}$	0.850	0.851	0.851	0.851	0.860	0.860
	$4f_{7/2}$	0.850	0.851	0.851	0.851	0.860	0.860
Ba^+	$4f_{5/2}$	3.420	3.498	3.497	3.498	3.652	4.019
	$4f_{7/2}$	3.420	3.496	3.498	3.499	3.652	3.992
La^{2+}	$4f_{5/2}$	7.959	13.145	14.175	16.250	17.662	18.279
	$4f_{7/2}$	7.956	12.963	14.038	16.057	17.461	18.094
Ce^{3+}	$4f_{5/2}$	16.637	31.054	32.395	35.005	36.401	36.748
	$4f_{7/2}$	16.571	30.743	32.150	34.711	36.112	36.468
Pr^{4+}	$4f_{5/2}$	32.389	52.071	53.507	56.368	57.723	57.512
	$4f_{7/2}$	32.191	51.643	53.157	55.970	57.339	59.137

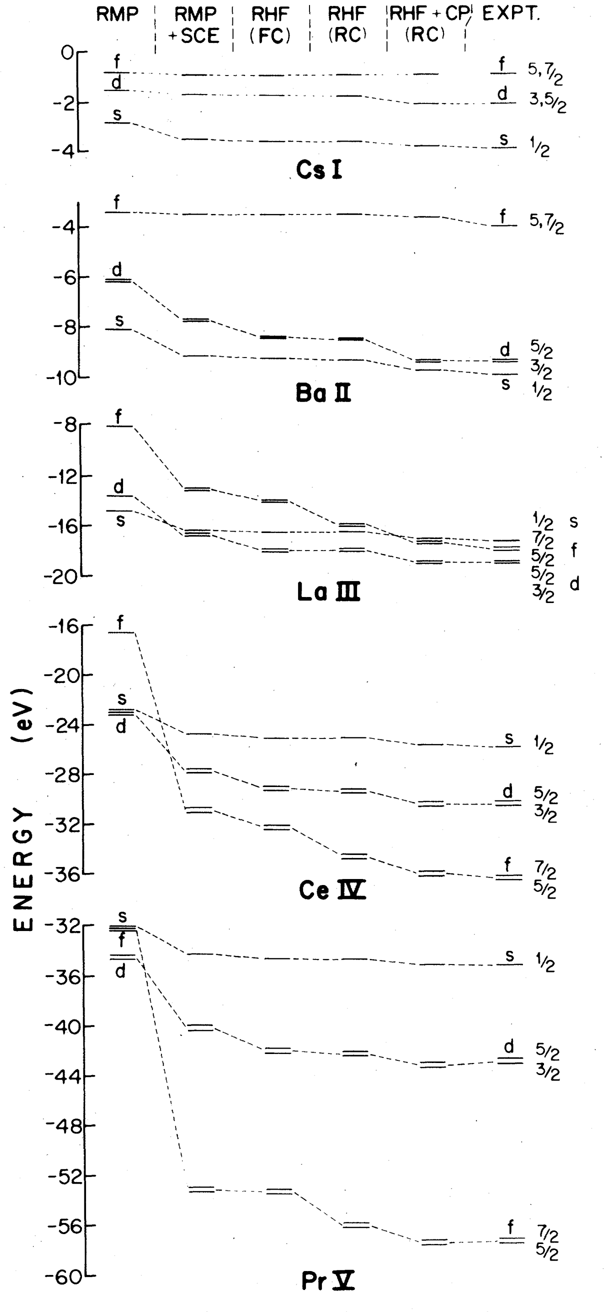

FIG. 5. Diagram of the $6s_{1/2}$, $5d_{3/2,5/2}$, and $4f_{5/2,7/2}$ energy levels for Cs through Pr^{4+} obtained with different theoretical methods and compared with experiment. The change in the ordering of levels as well as in the designation of ground state due to the influence of exchange effects on the eigenfunction is clearly visible. The influence of core relaxation and polarization can also be seen.

its maximum for the Ba^+ and Ce^{3+} systems, respectively, where the collapse phenomenon is most profound.

The role of core relaxation and polarization in the ionization potentials of $6s$, $5d$, and $4f$ states along the cesium sequence has been extensively discussed in our previous paper.[1] Here we should stress only that the unexpectedly large contribution of relaxation to ionization potentials of $4f_{5/2,7/2}$ states observed for La^{2+} and higher ionized members of the sequence seems to be entirely due to the collapse of the $4f$ orbital, which now becomes deeply embedded in the core of the system. Therefore, the relaxation of the core greatly affects the $4f$ electron, which now mostly resides inside the core (the average radius of the collapsed $4f_{7/2}$ state in La^{2+} is 1.241 a.u.). This is obviously not the case for Cs and Ba^+, where the $4f$ electron resides well outside the core (the mean radius is 17.967 and 8.292 a.u. for the $4f_{7/2}$ states in Cs and Ba^+, respectively) and the amplitude of the corresponding wave function is much smaller in the vicinity of the inner well of the effective potential than in the outer-well region. Therefore the contribution of the core relaxation to the $4f$ ionization potentials is virtually negligible for these systems.

It can also be seen from Table III that accounting for the influence of the valence-core electron exchange is crucial for the agreement between the theoretical fine-structure splittings and experimental data for the $5d$ and $4f$ levels in La^{2+} through Pr^{4+}. Further improvement is achieved when the nonlocal effects in exchange and the core relaxation are simultaneously accounted for and finally the remaining discrepancy is reduced to below 7% when the effect of core polarization is included. In Cs and Ba^+ the fine structure of the $5d$ and $4f$ states is very small, and for the $4f_{5/2,7/2}$ states of Cs it is even reversed, with the $5f_{7/2}$ state lying 2.2×10^{-5} eV below the $5f_{5/2}$ state. The reversal is evidently due to the strong influence of electron correlation, and is not predicted in either the model-potential or the restricted Hartree-Fock approaches employed here.

IV. CONCLUSIONS

We have demonstrated in this study that the effect of valence-core electron exchange on the valence electron wave functions is crucial for the proper ordering of theoretically determined $6s$, $5d$, and $4f$ energy levels for Cs through Pr^{4+} and for computations of the ionization potentials in good agreement with experiment, because the exchange effects greatly facilitate and make more sudden the collapse of $4f$ and $5d$ orbitals along the isoelectronic sequence. The exchange effects also largely improve the agreement of the $5d_{3/2,5/2}$ and $4f_{5/2,7/2}$ fine-structure splittings with experiment for La^{2+} through Pr^{4+}.

In the region of collapse, the properties of the $5d$ and $4f$ orbitals are unusually sensitive to small perturbations. Thus, the high accuracy of the representation adopted for the valence-core electron exchange as well as the nonlocal effects in exchange are much more important for the $4f$ and $5d$ orbitals, which undergo the collapse phenomenon, than for the relatively stable $6s$ orbitals. The core relaxation and polarization are, as already shown in our previous paper,[1] also very important for computations of accurate ionization potentials in the cesium isoelectronic sequence, particularly for the $5d$ and $4f$ states, as well as for calculations of their fine-structure splittings.

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