Collapse of *d* and *f* orbitals in the isoelectronic sequence of singly ionized ytterbium

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The phenomenon of ''collapse'' of $5d$ and $5f$ orbitals in the Yb^+ isoelectronic sequence occurring when the increasing Coulomb and exchange attractions overcome centrifugal repulsion is studied in this paper using both the relativistic model-potential and single-configuration Dirac-Fock techniques. As before for xenon and cesium sequences, valence-core electron exchange is found to play an essential role in the collapse phenomenon. Furthermore, the collapse greatly enhances the sensitivity of the properties of the orbitals that undergo this phenomenon to small changes in the effective potential, so that even much more subtle effects such as nonlocal exchange effects or core-valence electron correlation (core polarization) became more than usually important.

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I. INTRODUCTION

Lanthanide atoms and ions, because of the complexity of their spectra, are seldom the subject of intensive theoretical studies, despite vivid interest from astrophysicists, since the spectra of lanthanides are important in studies of evolution of some young stars, e.g., peculiar stars. However, for some of the rare earth systems, e.g., neutral and singly ionized ytterbium, a simple two- or one-electron spectrum appears to be superimposed on the complex many-electron spectra. Under this assumption we have studied in the past the energy levels and oscillator strengths in the spectra of neutral and singly ionized ytterbium as well as their isoelectronic sequences, using different theoretical techniques [1–4].

Formally, singly ionized ytterbium and systems isoelectronic to it belong to the thulium isoelectronic sequence. Unfortunately, no one-electron spectrum (i.e., spectrum with one valence electron outside the closed-shell core) has been discovered so far for neutral thulium, whose ground-state configuration is $4f^{13}5d6s$, in contrast to $4f^{14}6s$ which, due to competition between $4f$ and $5d$ orbitals ($n+l=7$ in both cases), occurs in Yb^+ and Lu^{2+}.

In Refs. [1–4] relativistic effects were treated accurately but electron correlations were included in a very approximate way through combining the core polarization model to represent the valence-core electron correlation with very modest multiconfiguration Dirac-Fock (MCDF) calculations to allow for the intravalence correlation, if required. This approach has been adopted recently by other authors for singly ionized ytterbium [5]; in addition, these authors carefully included the electron correlation at the expense of an approximate treatment of relativistic effects. This study, as well as the earlier one by Fawcett and Wilson [6] was restricted to the Yb II spectrum only, whereas our earlier studies [1–4] were devoted to Yb II isoelectronic systems and brought our attention to the gradual collapse of the *d* and *f* orbitals and its influence on both the energy level positions and oscillator strengths.

We have previously studied the collapse of $4f$ and $5d$ orbitals along the cesium isoelectronic sequence [7] as well as its influence on oscillator strengths for some low-lying transitions [8]. Earlier, Band *et al.* [9] studied formation of the collapsed $4f$ state in factitious ''Dirac-Fock atoms'' lanthanum and europium, whereas Cheng and Froese Fischer studied orbital collapse in the xenon isoelectronic sequence [10].

The present paper is devoted to a detailed study of the collapse of the lowest *d* and *f* orbitals in Yb II and its isoelectronic sequence. The behavior of the inner and outer wells of the effective potential along the sequence, as well as the way it is affected by the local valence-core electron exchange interaction and the core polarization by valence electrons are studied using the fully relativistic model-potential approach with no free parameters and the single-configuration self-consistent-field Dirac-Fock method.

It has to be stressed here that the relativistic model-potential approach is used in this study as an auxiliary tool only, in order to evaluate (through comparison between the model-potential and Dirac-Fock methods) the impact of the exchange interaction on the collapse phenomenon. In contrast to the Dirac-Fock scheme, where the nonlocal electron exchange is represented accurately, the model-potential approach allows one not only to omit the exchange interaction entirely but also to include it in an approximate way, e.g., through an *ab initio* local exchange model potential.

II. CALCULATIONS

As in our previous paper on collapse in the cesium isoelectronic sequence [7], we used here the relativistic model-potential (RMP) approach, discussed in detail in our earlier papers [11,12]. Three versions of this approach were used.

In the first (RMP) the valence electron is affected only by the core potential $V_c(r)$ which includes the nuclear attraction and Coulomb interelectronic repulsion,

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

where $\rho_c(r')$ is the radial electron density of the core (taken as computed in the Dirac-Fock approach for the parent ion) and Z is the charge of the nucleus (atomic units are employed in this paper). The electron exchange interaction is entirely omitted.

TABLE I. Core-polarization parameters: dipole polarizability α and cutoff radius r_0 (in a.u.).

System	α	r_0
Tm	9.97	1.574
Yb^+	6.39	1.492
Lu^{2+}	4.51	1.413
Hf^{3+}	3.34	1.342

In the second version (RMP + SCE) the local valence-core electron exchange interaction represented by the ''semiclassical exchange'' (SCE) potential V_{SCE}, proposed initially by Furness and McCarthy [13] and by Riley and Truhlar [14], is added to the core potential,

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

where $E<0$ is the energy of the valence electron and for doubly occupied spatial core orbitals

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

As can be seen from Eqs. (2) and (3), for bound states $(E<0)$ V_{SCE} becomes $-\beta/2$ as r approaches the classical turning point r_c, whereas for $r\gg r_c$ it increases and tends to E. Therefore V_{SCE} has to be cutoff shortly before the classical turning point and replaced by its value at this point, $-\beta/2$, which tends to zero at large r.

The SCE approximation does not depend on any empirical or adjustable parameter and turned out to be successful in our previous calculations [12].

In the third version (RMP + SCE + CP) the core polarization (CP) potential [11] V_{CP} is additionally included in the effective potential,

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

where α is the static dipole polarizability of the core and r_0 is the cutoff radius. For Yb II the α computed in a relativistic random-phase approximation (RRPA) calculation by Kolb *et al.* [15] was used, whereas for Lu III and Hf IV we employed the Hartree-Fock (HF) values of Fraga *et al.* [16] scaled down to include the relativistic effects at least partially. As the scaling factor we adopted the ratio $\alpha_{\mathrm{RRPA}}/\alpha_{\mathrm{HF}}=0.87$ computed employing the RRPA and HF values of α for Yb II from [15] and [16], respectively. The cutoff radius r_0 has been taken as the mean radius $\langle r\rangle$ of the outermost orbital of the core (see Table I).

To determine the influence of the nonlocal exchange effects on ionization potentials, single-configuration Dirac-Fock calculations, labeled DF(FC), were performed in the frozen core (FC) approximation using the parent ion of the system as the core. Such calculations differ from the RMP + SCE approximation only by accurate representation of the valence-core electron exchange interaction. Finally, the ionization potentials for different levels were computed in a single-configuration relaxed core [DF(RC)] approach with and without core polarization, which permits evaluation of the core-polarization and relaxation contributions.

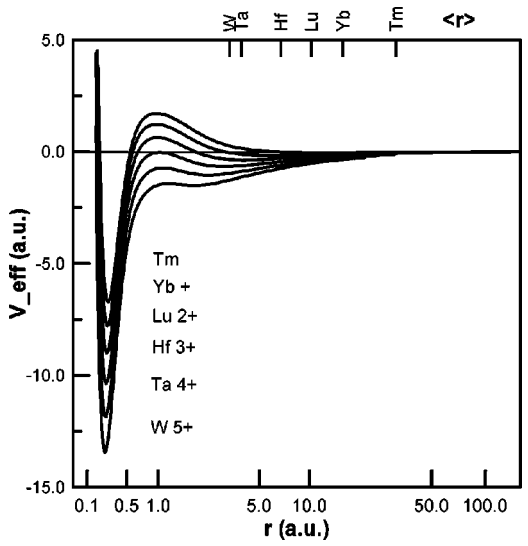

FIG. 1. The effective potential curves for $5f_{5/2}$ states in Tm through W^{5+} obtained using the relativistic model-potential approach with the valence-core electron exchange neglected (RMP). The mean radii $\langle r\rangle$ of the $5f_{5/2}$ orbitals are also marked. The horizontal scale is logarithmic.

The contribution of relativistic effects can also be found through comparison of DF(RC) results with those obtained in the nonrelativistic limit (NL) (i.e., computed with the velocity of light in a DF calculation tending to infinity). These are labeled NL-DF(RC).

III. DISCUSSION OF RESULTS

A. Orbital collapse

The phenomenon of orbital ''collapse'' is a rapid drop in the energy and size of a *d* or *f* orbital in response to change in the effective potential,

$$V_{eff}(r)=V(r)+\frac{l(l+1)}{2r^2}. \quad (5)$$

For sufficiently heavy atoms, V_{eff} has two wells separated by a barrier. As atomic number Z increases along the periodic table of atoms, the narrow inner well deepens and widens and the barrier drops slightly. When the barrier is sufficiently opaque, the two wells are clearly isolated and the inner well has little importance, until it is deep and wide enough to support a state below the eigenenergy of the isolated outer well. When this occurs, even in the presence of an opaque barrier, the orbital collapses from the outer well to the lower eigenstate of the inner well.

If one considers an isoelectronic sequence instead of the periodic table, the increasing charge of the ion core causes a rapid drop of the inner well and the barrier, but also deepens the outer well. In consequence, orbital collapse begins earlier and proceeds more gradually.

Figure 1 shows the effective potential V_{eff} for $5f_{5/2}$ orbitals in the Yb II isoelectronic sequence obtained in our RMP calculations with the valence-core electron exchange ne-

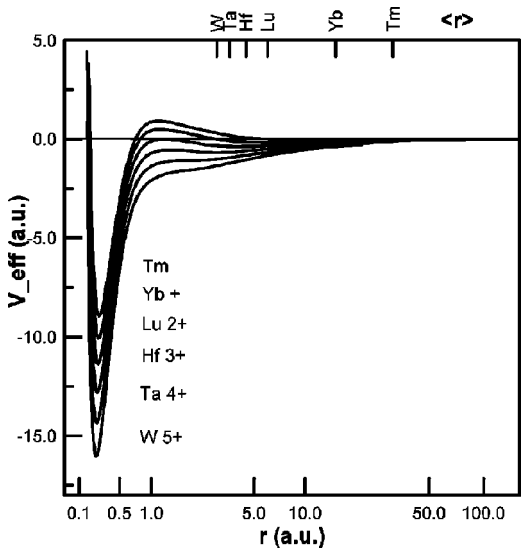

FIG. 2. As in Fig. 1, but the relativistic model-potential approach with valence-core electron exchange included in the semiempirical approximation (RMP + SCE) has been used.

glected. The $V_{eff}(r)$ for $5f_{7/2}$ orbitals are identical to those of $5f_{5/2}$. Figure 2 shows the effective potentials for $5f_{5/2}$ orbitals but with the core-valence electron exchange included in the semiclassical exchange approximation described above. Now the V_{eff} for $5f_{7/2}$ orbitals differ from those of $5d_{5/2}$ in Fig. 2 only by the dependence of the local exchange term on the one-electron eigenvalue, which is shown to be very small in Table II.

One can easily see from Figs. 1 and 2 as well as from Table II the deepening of both inner and outer wells as well as the lowering of the potential barrier with increasing Z, leading to the collapse of the $5f$ orbital, which can be followed in the average orbital radii indicated at the top of both figures. Comparison of Figs. 1 and 2 as well as Table II demonstrates the impact of the core-valence exchange in the

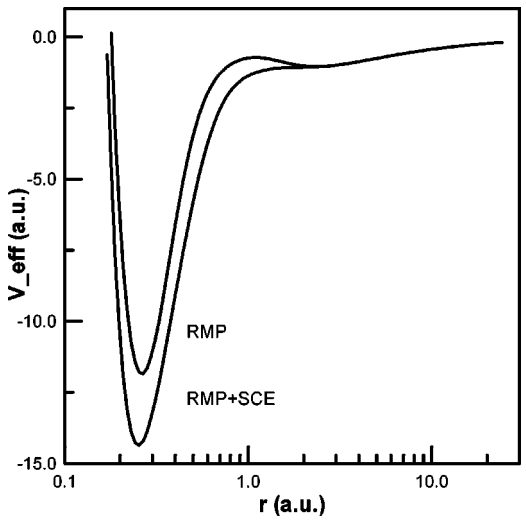

FIG. 3. Comparison of the effective potential curves obtained for the $5f_{5/2}$ state in Ta^{4+} using the model potential without (RMP) and with (RMP + SCE) the valence-core exchange included.

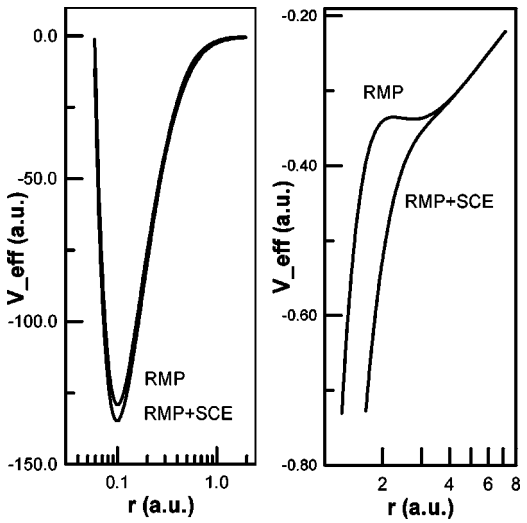

FIG. 4. As in Fig. 3, but the effective potential curves correspond to the $5d_{3/2}$ state in Yb^+, shown for small and large r values separately.

V_{eff} potentials for $5f_{5/2}$ orbitals along the Yb II isoelectronic sequence. The exchange interaction visibly enlarges the depth of the inner well by an amount that slowly increases along the sequence, whereas the outer well is only slightly affected. The height of the centrifugal barrier is also greatly lowered and the barrier itself disappears starting from Ta^{4+} if the exchange is included in the effective potential.

The effective potentials for the $5d_{3/2,5/2}$ orbitals have 10 to 18 times deeper inner wells than those of the $5f_{5/2,7/2}$ because of a smaller angular momentum and, in consequence, a smaller centrifugal repulsive part of the potential in Eq. (5). A tiny barrier (and in consequence a shallow outer well) can be seen for d states only for Yb^+ and only when the core-valence exchange is neglected. If it is included, even in rather crude SCE approximation, the outer well disappears completely.

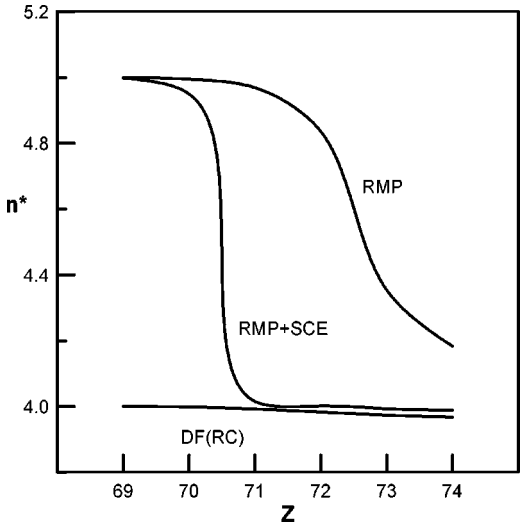

FIG. 5. Dependence of effective quantum number n^* on Z for $5f_{5/2}$ state along the thullium isoelectronic sequence.

TABLE II. The depth of the inner well (D_{inn}) and outer well (D_{out}) and the height of the centrifugal barrier (H_{barr}), as well as the resulting increase in the depths of the wells (ΔD_{inn} and ΔD_{out}) and the decrease in the height of the centrifugal barrier (ΔH_{barr}) due to exchange contribution and core polarization. Computed in the model-potential approach without (RMP) and with semiclassical exchange term (RMP + SCE) and with core polarization included (RMP + SCE + CP) (in eV).

System and state		D_{inn} (eV)				
		RMP	RMP + SCE	ΔD_{inn}	RMP + SCE + CP	ΔD_{inn}
Tm	$5d_{3/2}$	3369.57	3521.24	151.67	3521.33	0.09143
	$5d_{5/2}$	3369.57	3521.24	151.67	3521.33	0.09116
Yb^{+}	$5d_{3/2}$	3516.12	3669.85	153.73	3669.93	0.07374
	$5d_{5/2}$	3516.12	3669.85	153.73	3669.92	0.07374
Lu^{2+}	$5d_{3/2}$	3671.92	3829.96	158.04	3830.03	0.07211
	$5d_{5/2}$	3671.92	3829.95	158.03	3830.02	0.07211
Hf^{3+}	$5d_{3/2}$	3832.78	3989.68	156.90	3989.75	0.07211
	$5d_{5/2}$	3832.78	3989.67	156.89	3989.74	0.07211
Ta^{4+}	$5d_{3/2}$	3995.34	4160.12	164.77		
	$5d_{5/2}$	3995.34	4160.11	164.76		
W^{5+}	$5d_{3/2}$	4169.54	4333.58	164.04		
	$5d_{5/2}$	4169.54	4333.56	164.02		
Tm	$5f_{5/2}$	183.303	243.641	60.338	244.244	0.6028
	$5f_{7/2}$	183.303	243.641	60.338	244.244	0.6028
Yb^{+}	$5f_{5/2}$	211.926	274.199	62.273	274.701	0.5019
	$5f_{7/2}$	211.926	274.197	62.272	274.699	0.5019
Lu^{2+}	$5f_{5/2}$	245.443	309.892	64.449	310.379	0.4874
	$5f_{7/2}$	245.443	309.891	64.448	310.378	0.4874
Hf^{3+}	$5f_{5/2}$	282.561	348.692	66.130	349.144	0.4525
	$5f_{7/2}$	282.561	348.691	66.130	349.143	0.4525
Ta^{4+}	$5f_{5/2}$	322.591	391.026	68.434		
	$5f_{7/2}$	322.591	391.025	68.433		
W^{5+}	$5f_{5/2}$	366.139	435.924	69.785		
	$5f_{7/2}$	366.139	435.922	69.783		

System and state		H_{barr} (eV)				
		RMP	RMP + SCE	ΔH_{barr}	RMP + SCE + CP	ΔH_{barr}
Tm	$5d_{3/2}$	4.8612	0.8708	−3.9904	0.2988	−0.5720
	$5d_{5/2}$	4.8612	0.8717	−3.9896	0.3001	−0.5716
Yb^{+}	$5d_{3/2}$	0.0749				
	$5d_{5/2}$	0.0749				
Lu^{2+}	$5d_{3/2}$					
	$5d_{5/2}$					
Hf^{3+}	$5d_{3/2}$					
	$5d_{5/2}$					
Ta^{4+}	$5d_{3/2}$					
	$5d_{5/2}$					
W^{5+}	$5d_{3/2}$					
	$5d_{5/2}$					
Tm	$5f_{5/2}$	47.541	26.0394	−21.5013	23.2857	−2.7537
	$5f_{7/2}$	47.541	26.0394	−21.5013	23.2857	−2.7537
Yb^{+}	$5f_{5/2}$	37.565	18.3746	−19.1900	15.8835	−2.4912
	$5f_{7/2}$	37.565	18.3820	−19.1826	15.8909	−2.4912
Lu^{2+}	$5f_{5/2}$	27.078	10.1543	−16.9235	8.2251	−1.9292
	$5f_{7/2}$	27.078	10.1570	−16.9208	8.2278	−1.9291
Hf^{3+}	$5f_{5/2}$	17.231	3.5279	−13.7036	2.3043	−1.2235
	$5f_{7/2}$	17.231	3.5306	−13.7008	2.3069	−1.2238
Ta^{4+}	$5f_{5/2}$	8.635				

TABLE II. (*Continued*).

System and state		D_{inn} (eV) RMP	RMP + SCE	ΔD_{inn}	RMP + SCE + CP	ΔD_{inn}
	$5f_{7/2}$	8.635				
W^{5+}	$5f_{5/2}$	2.178				
	$5f_{7/2}$	2.178				

System and state		D_{out} (eV) RMP	RMP + SCE	ΔD_{out}	RMP + SCE + CP	ΔD_{out}
Tm	$5d_{3/2}$	2.2676	2.2734	0.0058	2.3790	0.1056
	$5d_{5/2}$	2.2676	2.2733	0.0057	2.3789	0.1056
Yb^+	$5d_{3/2}$	9.1930				
	$5d_{5/2}$	9.1930				
Lu^{2+}	$5d_{3/2}$					
	$5d_{5/2}$					
Hf^{3+}	$5d_{3/2}$					
	$5d_{5/2}$					
Ta^{4+}	$5d_{3/2}$					
	$5d_{5/2}$					
W^{5+}	$5d_{3/2}$					
	$5d_{5/2}$					
Tm	$5f_{5/2}$	1.1332	1.1332	0.0000	1.1400	0.0068
	$5f_{7/2}$	1.1332	1.1332	0.0000	1.1400	0.0068
Yb^+	$5f_{5/2}$	4.5330	4.5331	0.0001	4.5938	0.0608
	$5f_{7/2}$	4.5330	4.5331	0.0001	4.5938	0.0608
Lu^{2+}	$5f_{5/2}$	10.2028	10.2084	0.0056	10.3855	0.1771
	$5f_{7/2}$	10.2028	10.2084	0.0056	10.3855	0.1771
Hf^{3+}	$5f_{5/2}$	18.1503	18.2237	0.0735	18.5999	0.3762
	$5f_{7/2}$	18.1503	18.2236	0.0734	18.5998	0.3761
Ta^{4+}	$5f_{5/2}$	28.4306				
	$5f_{7/2}$	28.4306				
W^{5+}	$5f_{5/2}$	41.2844				
	$5f_{7/2}$	41.2844				

The influence of the exchange on the shape of the effective potential curve may be seen more closely in Figs. 3 and 4, which depict potential curves without and with the exchange for the $5f_{5/2}$ state in Ta^{4+} and the $5d_{3/2}$ in Yb^+, respectively.

Table III shows the relative orbital contraction due to the exchange. It reaches 30% to 40% for orbitals in the systems where collapse is under way and decreases (for f states even abruptly) when the collapse has already occurred. One should note an unexpectedly large influence of the nonlocal exchange effects, otherwise unimportant, on orbital contraction for the $5f_{5/2,7/2}$ states in Yb^+, which dominate the exchange contribution. This was not observed before for the Cs sequence and suggests that the simple local exchange approximation SCE is not able to adequately describe the collapse phenomenon in this case.

Table II also shows the effect of the core polarization on the inner and outer wells and potential barrier. Though the core polarization also tends to deepen both the inner and outer wells and lower the barrier, its influence on the inner well and the barrier is marginal and in no way can be compared with the unique role played in this case by the core-valence exchange. However, for the outer well the influence of the core polarization, though also very weak, exceeds that of the exchange effect. This is due to the short-range nature of exchange effects, which are virtually negligible in the outer well dominated by the long-range Coulomb potential.

Table IV shows the ionization potentials computed using the relativistic model-potential approach without (RMP) and with (RMP + SCE) local valence-core electron exchange, as well as by employing the relativistic single-configuration Dirac-Fock method in the frozen parent-ion-like core approximation [DF(FC)] (i.e., with accurate nonlocal exchange) and the relaxed core approximation without [DF(RC)] and with [DF(RC) + CP] the core polarization included. The unexpectedly large impact of the nonlocal exchange observed previously in orbital contraction for the $5f_{5/2,7/2}$ states in Yb^+ is reflected here in the ionization potentials for those states evaluated in the RMP + SCE and DF(FC) approaches, which differ in the accuracy of exchange representation (cf. Table III). Such sensitivity to the exchange suggests that $5f$ orbital collapse is well advanced

TABLE III. The relative contribution of local (a) and nonlocal (b) exchange to ionization potentials (I) along the Yb^+ isoelectronic sequence as well as the relative contraction of orbitals due to exchange (X) for various methods of calculation. Description of columns: (a) $X=$RMP + SCE, (b) X = DF(FC). Values given in percent.

System and state		$100(I_X-I_{RMP})/I_X$ (a)	(b)	$100(\langle r\rangle_{RMP}-\langle r\rangle_X)/\langle r\rangle_{RMP}$ (a)	(b)
Tm	$5d_{3/2}$	6.29	5.42	12.8	11.1
	$5d_{5/2}$	5.86	5.96	11.8	12.0
Yb^+	$5d_{3/2}$	21.8	23.6	32.8	34.7
	$5d_{5/2}$	20.3	23.4	31.0	34.1
Lu^{2+}	$5d_{3/2}$	22.2	24.5	27.1	29.0
	$5d_{5/2}$	21.1	24.2	26.2	28.6
Hf^{3+}	$5d_{3/2}$	19.6	21.8	21.3	23.0
	$5d_{5/2}$	18.8	21.6	20.8	22.8
Ta^{4+}	$5d_{3/2}$	17.2	19.2	17.2	18.8
	$5d_{5/2}$	16.5	19.0	16.9	18.7
W^{5+}	$5d_{3/2}$	15.2	17.0	14.3	15.9
	$5d_{5/2}$	14.7	16.9	14.1	15.8
Tm	$5f_{5/2}$	0.040	36.0	0.076	42.8
	$5f_{7/2}$	0.042	36.0	0.073	42.8
Yb^+	$5f_{5/2}$	1.79	35.9	4.48	42.8
	$5f_{7/2}$	1.40	35.9	3.22	42.7
Lu^{2+}	$5f_{5/2}$	34.7	35.4	41.1	42.0
	$5f_{7/2}$	34.5	35.4	40.9	42.0
Hf^{3+}	$5f_{5/2}$	31.6	32.2	34.0	34.9
	$5f_{7/2}$	31.7	32.4	34.5	35.5
Ta^{4+}	$5f_{5/2}$	15.9	16.7	8.30	9.48
	$5f_{7/2}$	17.0	17.9	8.83	10.2
W^{5+}	$5f_{5/2}$	9.13	9.98	9.95	11.1
	$5f_{7/2}$	9.53	10.5	9.92	11.2
Tm	$6s_{1/2}$	22.4	16.7	20.6	16.3
Yb^+	$6s_{1/2}$	15.1	13.3	14.2	12.5
Lu^{2+}	$6s_{1/2}$	11.9	11.1	11.0	10.2
Hf^{3+}	$6s_{1/2}$	9.86	9.54	9.04	8.62
Ta^{4+}	$6s_{1/2}$	8.46	8.39	7.68	7.48
W^{5+}	$6s_{1/2}$	7.43	7.50	14.9	14.8

already in singly ionized ytterbium.

In order to confirm this suspicion, we generated the $4f^{14}6s$, $4f^{14}5d$, and $4f^{14}5f$ states for neutral thulium (not observed so far), using both relativistic model-potential and single-configuration Dirac-Fock techniques. The results have been included in Tables II, III, and IV. As can be seen from the relative contraction of average orbital radii $\langle r\rangle$ presented in Table III, the $5f$ collapse is virtually completed in neutral thulium and nonlocal exchange effects are even more important there than in Yb^+. This is further corroborated by Fig. 5, which presents the dependence of the effective quantum number n^* on Z. It can clearly be seen that the model-potential approach with local exchange (RMP + SCE) predicts full collapse of the $5f_{5/2}$ orbital only for $Z=71$ (Lu^{2+}), whereas the Dirac–Fock method with accurate nonlocal exchange proves that this effect occurs as early as for $Z=69$ (neutral Tm). (The n^* value for $5f_{5/2}$ computed with the Dirac-Fock method is 4 already for thullium, which confirms that this orbital is a ''collapsed'' one for the entire isoelectronic sequence; cf. Fig. 5.)

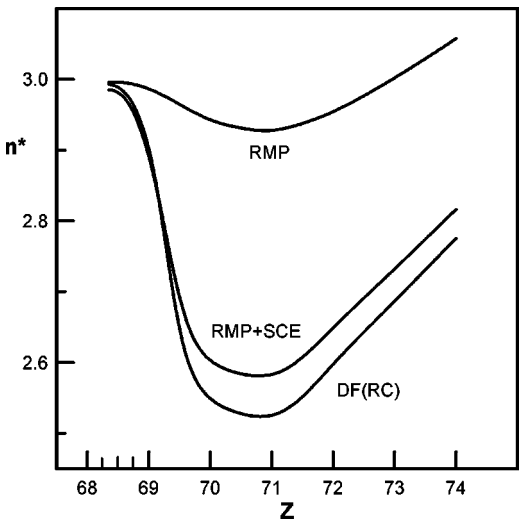

FIG. 6. Dependence of effective quantum number n^* on Z for $5d_{3/2}$ state along the thullium isoelectronic sequence.

Table III suggests also that collapse of $5d$ orbitals occurs fully only in singly ionized ytterbium. To elucidate the behavior of the $5d_{3/2}$ orbital even more closely we performed additional model-potential and Dirac-Fock calculations for this orbital in systems with noninteger Z values smaller than 69. The results, presented in Fig. 6, demonstrate that collapse of the $5d_{3/2}$ orbital is already well advanced in neutral Tm ($Z=69$) and seems to be most profound for Yb^+ ($Z=71$) and Lu^{2+} ($Z=71$). This is further corroborated by results of our calculations presented in Table II, which show that the centrifugal barrier experienced by $5d$ electrons disappears completely as soon as for Yb^+ if only exchange effects are accounted for, whereas the depth of the inner well (which is, in fact, 20 times deeper than for $5f$ electrons) increases along the sequence. On the other hand, the increase in n^* observed in Fig. 6 for more highly ionized systems may lead to some doubts whether the collapse of $5d$ orbitals is indeed entirely completed for Lu^{2+}. Figure 6 shows also that, in contrast to the case of the $5f_{5/2}$ orbital, the nonlocal exchage effects are not essential here, as both the model-potential RMP + SCE and Dirac-Fock methods exhibit very similar behavior.

Our calculation predicts that, beginning from Hf^{3+}, the $5d_{3/2}$ state becomes the ground state instead of $6s_{1/2}$. As can be seen from Table IV it is entirely at the expense of the exchange interaction. Inclusion of exchange even in an approximate way greatly improves the agreement of theoretical and experimental ionization potentials. A further improvement is observed as accurate nonlocal exchange, core relaxation, and finally core polarization are added in the DF(FC), DF(RC), and DF(RC) + CP calculations, respectively.

B. Ionization potentials

Figures 7(a)–7(e) show contributions to the ionization potentials along the Yb^+ isoelectronic sequence (to Ra^{19+}) of

TABLE IV. Comparison of ionization potentials for some levels in the Yb^+ isoelectronic sequence, obtained neglecting the exchange effect (RMP) as well as including local exchange (RMP + SCE), nonlocal exchange [DF(FC)], core relaxation [DF(RC)] and core polarization [DF(RC) + CP]. Experimental data taken from [21]. Values given in eV.

System and state		Ionization potentials						
		RMP	RMP + SCE	NL-DF(RC)	DF(FC)	DF(RC)	DF(RC) + CP	Experiment
Tm	$5d_{3/2}$	1.526	1.628	1.630	1.613	1.615	1.794	
	$5d_{5/2}$	1.525	1.620	1.630	1.622	1.624	1.807	
Yb^+	$5d_{3/2}$	6.285	8.032	8.748	8.228	8.376	9.328	9.3371
	$5d_{5/2}$	6.257	7.849	8.746	8.173	8.309	9.220	9.1670
Lu^{2+}	$5d_{3/2}$	14.284	18.354	19.798	18.912	19.202	20.308	20.2519
	$5d_{5/2}$	14.155	17.930	19.795	18.668	18.930	19.998	19.8873
Hf^{3+}	$5d_{3/2}$	24.945	31.032	32.987	31.898	32.272	33.398	
	$5d_{5/2}$	24.651	30.357	32.985	31.434	31.774	32.867	
Ta^{4+}	$5d_{3/2}$	37.751	45.574	47.916	46.702	47.134		
	$5d_{5/2}$	37.252	44.631	47.914	45.997	46.392		
W^{5+}	$5d_{3/2}$	52.400	61.764	64.414	63.122	63.600		
	$5d_{5/2}$	51.664	60.535	64.413	62.156	62.594		
Tm	$5f_{5/2}$	0.544	0.545	0.850	0.850	0.850	0.855	
	$5f_{7/2}$	0.544	0.545	0.850	0.850	0.850	0.855	
Yb^+	$5f_{5/2}$	2.181	2.221	3.407	3.404	3.404	3.442	3.4426
	$5f_{7/2}$	2.181	2.212	3.407	3.403	3.404	3.442	3.4330
Lu^{2+}	$5f_{5/2}$	4.959	7.595	7.706	7.681	7.683	7.791	7.8679
	$5f_{7/2}$	4.958	7.572	7.706	7.680	7.682	7.789	7.8538
Hf^{3+}	$5f_{5/2}$	9.305	13.595	13.809	13.718	13.723	13.923	
	$5f_{7/2}$	9.269	13.566	13.809	13.714	13.719	13.919	
Ta^{4+}	$5f_{5/2}$	17.932	21.332	21.746	21.526	21.541		
	$5f_{7/2}$	17.663	21.282	21.746	21.514	21.529		
W^{5+}	$5f_{5/2}$	27.978	30.790	31.493	31.080	31.111		
	$5f_{7/2}$	27.780	30.707	31.493	31.052	31.084		
Tm	$6s_{1/2}$	3.513	4.525	3.892	4.220	4.241	4.650	
Yb^+	$6s_{1/2}$	9.742	11.473	10.518	11.232	11.269	11.758	12.184
Lu^{2+}	$6s_{1/2}$	17.686	20.065	18.708	19.890	19.945	20.470	20.96
Hf^{3+}	$6s_{1/2}$	27.054	30.012	28.187	29.907	29.977	30.518	
Ta^{4+}	$6s_{1/2}$	37.699	41.183	38.823	41.152	41.235		
W^{5+}	$6s_{1/2}$	49.530	53.505	50.535	53.548	53.643		

relativistic effects, relaxation, and core polarization for the $6s_{1/2}$ (a), $6p_{1/2}$ (b), $6p_{3/2}$ (c), $5d_{3/2}$ (d), and $5f_{5/2}$ (e) states. The contribution of relativistic effects is positive and fairly large, strongly increasing along the sequence for $6s_{1/2}$ and $6p_{1/2}$ states, whereas for the $6p_{3/2}$ state it is about one order of magnitude smaller, as expected (see below). For $5f_{5/2}$ orbitals the relativistic contribution is negative all along the part of the sequence under consideration. For $5d_{3/2}$ states it is negative at first and changes sign to positive near Bi^{14+}.

The negative contribution of the relativistic effects for the $nd_{3/2}$ and $nf_{5/2}$ ionization potentials can be easily explained. As found by Desclaux and Kim [17] and Rose *et al.* [18], the relativistic effect on the valence electron orbital results from competition of two effects. The first, direct, is due to the relativistic form of the one-electron Hamiltonian of the valence electron and causes contraction of the orbital and a positive contribution to the ionization potential (the orbital is more strongly bound). The second effect (indirect) results from the relativistic contraction of the inner orbitals and leads to better screening of the nuclear charge experienced by the valence electron and, in consequence, to dilatation of the valence electron orbital. The direct effect (contraction) dominates for the valence $ns_{1/2}$ and $np_{1/2}$ orbitals, for $np_{3/2}$ direct and indirect effects virtually cancel each other, whereas for $nd_{3/2,5/2}$ and even more for $nf_{5/2,7/2}$ the indirect effect prevails, resulting in more loosely bound electrons and a negative contribution to the ionization potential. As we can observe in Fig. 7(d) for the $5d_{3/2}$ orbital, first the indirect effect dominates, but for highly ionized systems the direct effect prevails again as could be expected for high-*Z* systems.

It has to be stressed that complete neglect of relativistic effects, as in our nonrelativistic limit DF calculation (NL-DF), may result—entirely due to cancellation of errors—in better agreement with experiment than is observed for fully relativistic DF results (cf. Table IV).

The contribution of core relaxation is almost always positive except for the $5f_{5/2}$ orbital in Yb^+ through Hf^{3+}, where

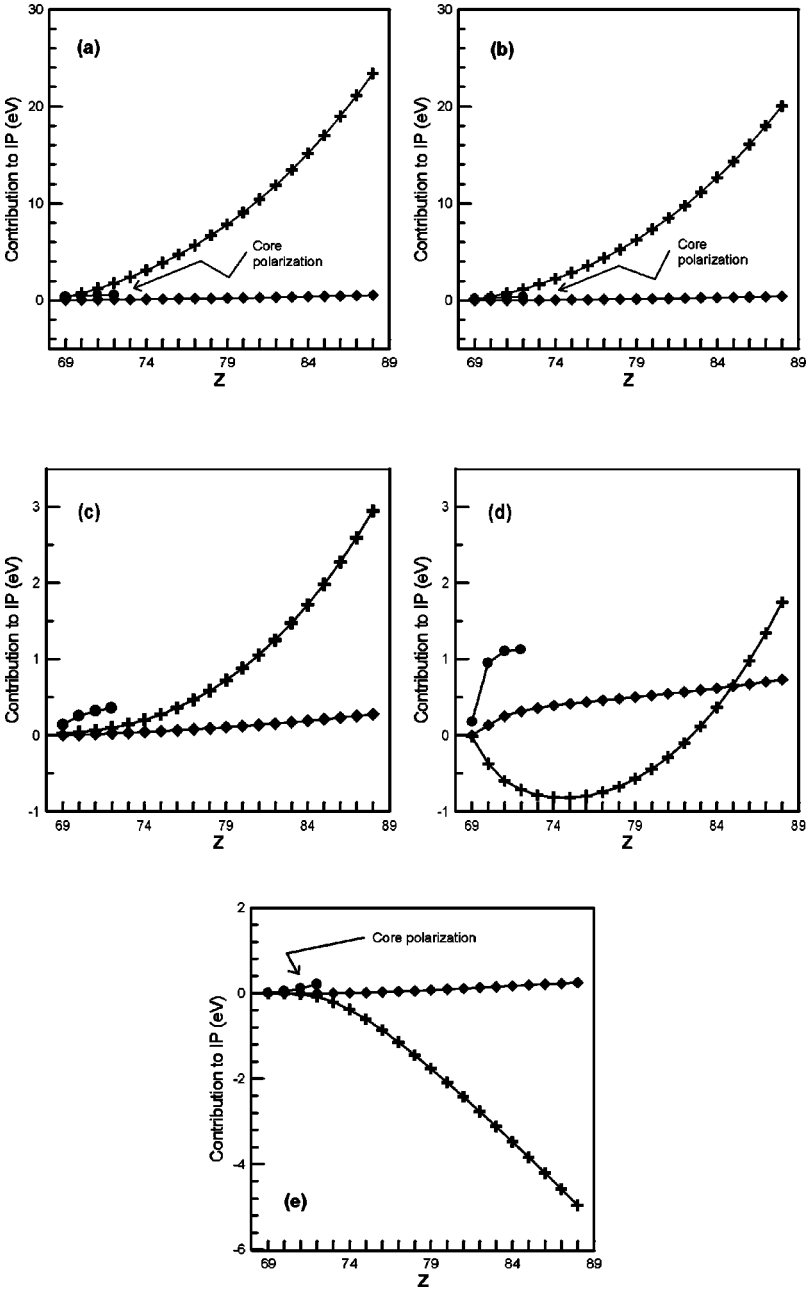

FIG. 7. Contribution to ionization potentials (in eV) along the Yb^{+} isoelectronic sequence (to Ra^{19+}) of relativistic effects (crosses), relaxation (diamonds), and core polarization (full circles) for $6s_{1/2}$ (a), $6p_{1/2}$ (b), $6p_{3/2}$ (c), $5d_{3/2}$ (d), and $5f_{5/2}$ (e) states.

it is also extremally small. This, in our opinion, is due to the fact that despite the eventual collapse the $5f_{5/2,7/2}$ orbitals for these systems are still fairly distant from the core. This is quite different from our earlier observations for La^{2+} through Pr^{4+} in the Cs sequence [19], where $4f_{5/2,7/2}$ orbitals mostly resided inside the core and the relaxation contribution was unexpectedly large. For $6s$, $6p$, and $5f$ orbitals, the core relaxation is smaller by an of order magnitude or even two than the relativistic effects, and only for $5d$ is it of the same order. It increases slowly along the isoelectronic sequence as relativistically contracted valence orbitals approach the core of the system.

The contribution of core polarization which, due to availability of the static dipole polarizabilities, could be evaluated for low ionization stages only, is positive, of the same order as the relativistic effect, and tends to increase along the isoelectronic sequence. This is probably due to an accompanying contraction of $\langle r \rangle$ along the sequence, which for d and f orbitals is enhanced by the collapse phenomenon.

C. Conclusions

We have demonstrated here the important role of the valence-core electron exchange in the collapse phenomenon of $5d$ and $5f$ orbitals along the Yb II isoelectronic sequence. As in the region of collapse the properties of $5d$ and $5f$ orbitals are unusually sensitive to changes in the effective potential, the high accuracy of the representation used for the valence-core electron exchange as well as the inclusion of nonlocal exchange effects are important for these orbitals. The collapse phenomenon also enhances the influence of the core polarization which, usually known to be the largest for

low-lying s or p orbitals, is here even more important for d orbitals, which undergo collapse in Yb^+ through Hf^{3+} systems.

Finally, one has to remember that, unlike the cesium sequence we studied previously [7], the one-electron spectrum in Yb^+ and systems isoelectronic to it is imposed on top of a complex spectrum. Our former studies [2] of fine structure splitting in Yb^+ and Lu^{2+} clearly demonstrate strong perturbation of $4f^{14}5f$ states, probably by the $4f^{13}5d6s$ configuration (cf. [20]), as the distance between these two configurations decreases when $4f^{13}5d6s$ is pushed up and $4f^{14}5f$ is lowered due to orbital collapse. Therefore the influence of the complex spectrum may somewhat obscure the collapse phenomenon for $5f$ orbitals. In contrast to that, the $5d$ orbitals in Yb^+ and Lu^{2+} are absolutely unperturbed and their purity according to Fawcett and Wilson [6] is over 99%.

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