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Term-Dependent Hybridization of the $5f$ Wave Functions of Ba and Ba^{++}

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It is shown that, unlike in neutral Ba, the $4d\to 5f$ transitions cannot be neglected in the interpretation of the $4d$ spectrum of Ba^{++}. A term-dependent hybridization of the $5f$ wave functions occurs, the effects of which reverse between Ba and Ba^{++}, and oscillator strength reappears in the $4d\to nf$ ($n\geq 5$) transitions. A second kind of wave-function collapse is identified and its effects are described.

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The formation and properties of the rare-earth elements have been explained[1] in terms of the transfer of the $4f$ wave function from the outer to the inner well of a double-valley potential. The sudden contraction of the $4f$ wave function (wave-function collapse) and consequent spatial segregation of nf solutions between the inner and outer wells, which occurs at about $Z=57$, leads to highly non-Rydberg $4d$-subshell spectra in the rare earths and preceding elements. In particular the spectra of these elements show very strong $4d\to 4f$ resonances while higher members of $4d\to nf$ series possess negligible oscillator strength. In neutral Ba prime interest attaches to the transition to the $4d^9 4f 6s^2\,{}^1P_1$ upper state which is the only $4d\to 4f$ transition allowed by LS selection rules for electric dipole excitation. The ${}^1P$ resonance is placed in the continuum following the $4d$ ionization threshold by SCF (self-consistent-field) configuration-average calculations and is better described[2] as $4d\to(4+\epsilon)f\,{}^1P_1$, this notation indicating that the $4f\,{}^1P$ and $\epsilon f\,{}^1P$ wave functions are hybridized.

In a recent experiment[3] photoexcitation of the $4d$ subshell in the species Ba, Ba^+, and Ba^{++} has been observed. Thus qualitative changes in the spectral distribution of oscillator strength with increasing stage of ionization can be followed experimentally. However, the interpretation of the Ba^{++} spectrum presents difficulties, where more discrete structure exists than might be expected. The present Letter makes a start on this complex problem. We point out that, in contrast to the situations which have previously been analyzed,[4] the $d\to f$ channel in Ba^{++} *is not entirely dominated* by the $4d\to(4+\epsilon)f\,{}^1P_1$ transition. Indeed, the $4d\to 5f$ transitions possess significant oscillator strength—superior to that of the

$4d \to 4f$ triplet transitions and also superior to that of the $4d \to np$ transitions.

We have thus been led to study the nf wave functions with $n > 4$ in Ba, Ba^+, and Ba^{++}. Our study has revealed surprising properties, which are quite different from those previously described for cases involving wave-function collapse. For example, when the $5f$ wave function is expelled further into the outer valley of the double-valley potential, it can happen that its spatial overlap with the $4d$ core actually *increases*. Thus, the argument that solutions can be partitioned according to whether they are eigenstates of the inner or of the outer well must be treated with great caution *even in cases where 4f collapse has clearly occurred.* The strong term dependence of the resulting anomalies also precludes atomic structure calculations by the usual method of energy-matrix diagonalization.

A Hartree-Slater SCF[5] Ba^{++} $4d^{10} \to 4d^9(4f \times 5f \times 6f \times 6p)$ calculation has been performed and salient results are collected in Table I. Note that this calculation, which includes configuration mixing and relativistic corrections, does not take account of the term dependence of the wave functions (the relevance of which is emphasized below) and does not treat interactions with the continuum. Nevertheless, an important point emerges from Table I: The $4d^9 5f$ states of Ba^{++} possess significant gf values (statistically weighted oscillator strengths) and also contain appreciable admixtures of $4d^9 4f\,^1P_1$ character. The oscillator strengths of the $4d \to 5f$ transitions are in fact larger in our calculation than those of the $4d \to 4f$ triplet transitions, because $4d^9 4f$ is quite closely LS coupled. The calculation also shows that the $6f$ transitions are stronger than the $6p$ transitions. A separate Hartree-Slater calculation *without* configuration mixing has shown that the significant intensities of the $4d \to 5f$ transitions are an intrinsic property rather than a consequence of configuration mixing.

TABLE I. Ba^{++} $4d^{10}$–$4d^9(4f \times 5f \times 6f \times 6p)$ results.

λ (Å)	gf	Purity	Upper State(J=1)	% $4d^9$ ^1P component
135.440	0.0029	98%	$4d^9$ 4f ^3P	0.04
129.800	0.0255	96%	$4d^9$ 4f ^3D	0.34
125.440	0.0500	99.7%	$4d^9$ 6p (2½,1½)	0.003
122.683	0.0372	92%	$4d^9$ 6p (1½,½)	0.004
122.235	0.0009	92%	$4d^9$ 6p (1½,1½)	0.0007
118.899	0.2364	88%	$4d^9$ 5f (2½,3½)	9.4
118.553	0.0053	99%	$4d^9$ 5f (2½,2½)	0.22
116.148	0.3298	62%	$4d^9$ 5f (1½,2½)	8.6
115.519	0.0102	62%	$4d^9$ 6f (2½,3½)	0.17
115.438	0.0033	78%	$4d^9$ 6f (2½,2½)	0.06
112.938	0.1762	94%	$4d^9$ 6f (1½,2½)	2.9
104.675	10.8781	78%	$4d^9$ 4f ^1P	78.3

It thus emerges that the higher nf rather than any np states are crucial to the interpretation of the Ba^{++} spectrum. We have therefore studied the evolution of the nf wave functions from Ba to Ba^{++} paying special attention to term dependence and to their behavior in the inner well. For technical reasons term dependence of the radial wave functions is not easily inserted in the Hartree-Slater calculations so that, to investigate this effect, we have performed single-configuration nonrelativistic Hartree-Fock SCF calculations.[6] Effective radial potentials have also been extracted.

The results of this second group of calculations are summarized in Table II. In neutral Ba, as Wendin[7] has emphasized, the $4f$ wave function of $4d^9 4f$ in the configuration-average approximation ($4f_{av}$) is collapsed, but the ^1P $4f$ wave function is external to the potential barrier. Collapse of this first kind, which is characteristic of elements in which collapse is beginning to occur, produces a non-Rydberg spectrum with a very strong $4d \to 4f$ resonance above the ionization threshold and quenching of the rest of the $4d \to nf$ series. As the inner-well potential becomes more attractive between Ba and Ba^{++} a second kind of wave-function collapse occurs. In the second kind of collapse, the $4f\,^1P$ wave function falls into the inner well producing a very strong resonance below threshold and other effects which are somewhat different from those experienced in the first kind of collapse. In particular, the character of the ^1P $(4+\epsilon)f$ resonance is expected to change as the $(4+\epsilon)f$ wave function turns into a bound $4f$ wave function. However, our calculations do not include continuum states and we therefore concentrate on the nf ($n \geq 5$) wave functions.

The calculations reveal a marked tendency of nf ($n \geq 5$) wave functions to become hybrids (i.e., simultaneous eigenfunctions of both wells with comparable amplitude on both sides of the potential barrier). Examples are plotted in Fig. 1. Similar behavior has previously been found in

TABLE II. Summary of single-configuration $4d^9nf$ calculations.

Species/Configuration		$4d^9nf$ ^1P solutions $F^2(4dnf)$	$\langle r \rangle$	Inner Well Depth	Potential Barrier	Configuration average solutions $F^2(4dnf)$	$\langle r \rangle$	Inner Well Depth	Potential Barrier	F^2 $^1P/F^2_{AV}$
Ba	$4d^9 4f 6s^2$	0.000347	17.49	-7.38	large	0.435	1.17	- 9.59	small	0.0008
Ba^+	$4d^9 4f 6s$	0.00766	7.53	-7.92	large	0.436	1.17	- 9.98	none	0.018
Ba^{++}	$4d^9 4f$	0.0317	4.69	-8.51	small	0.438	1.16	-10.45	none	0.072
Ba	$4d^9 6s^2 5f$	0.000204	30.69	-7.38	large	0.0110	24.63	- 8.78	large	0.018
Ba^+	$4d^9 6s 5f$	0.00556	13.64	-7.92	large	0.00790[a] 0.0489[a]	8.71 9.15	- 9.21 - 9.33	small small	0.70 0.11
Ba^{++}	$4d^9 5f$	0.0242	8.51	-8.53	small	0.0195	6.19	- 9.76	small	1.25
Ba^{+++}	$4d^9 5p^5 5f$	0.0556	5.79	-9.67	small	0.0337	4.67	-10.80	none	1.65
Ba	$4d^9 6s^2 6f$	0.000127	46.95	-7.39	large	0.00404	38.58	- 8.77	large	0.031
Ba^{++}	$4d^9 6f$	0.0147	13.56	-8.52	small	0.0101	10.74	- 9.72	small	1.46

[a]Alternative solutions (see text).

Ba^+ without a $4d$ vacancy but, to our knowledge, has never been described in a case where $4f$ wave-function collapse has occurred. The strong term dependence of the hybrid orbitals should also be noted, because of its effect on any attempt to calculate the energy matrix by the usual Slater-Condon approach which would leave certain off-diagonal elements undefined. This arises because the radial and angular solutions to the Schrödinger equation cease to be independent, as the large variation of Slater-Condon integrals (Table II) demonstrates.

Previous calculations of the $5f$ wave functions have concentrated on neutral Ba, where the tendency to form hybrids is confined to $5f_{av}$ and therefore does not affect the transition probability. Wendin[7] has described how the $^1P\,4f$ wave function lies energetically and spatially very close to $5f_{av}$ outside the potential barrier. In the course of his and ensuing discussion[7,8] of the behavior of the $4f$ functions in the ^1P and configuration-average potentials, some $5f_{av}$ functions were presented which differ somewhat from those in the present work.

The usual method of facilitating convergence for "difficult" cases in self-consistent field calculations, namely performing a sequence of calculations in the sense of decreasing hydrogenicity down an isoelectronic sequence, often fails when there is wave-function collapse. This occurs because, when the final solution is a hybrid function, the ratio of the amplitudes in each well varies quickly with nuclear charge. In such conditions, it is important to allow *all* the wave functions to vary, since small changes of effective potential can precipitate large variations of the wave function, a point which is emphasized by our results for the $5f_{av}$ wave function of Ba^+. Two Hartree-Fock calculations, performed with only slightly differing prescriptions as to the sequence of the calculations, have produced different results at convergence (Table II) and it is unclear from the usual tests of quality which of the two is the "best" solution. Fortunately the problem occurs only in this particular instance.

In neutral Ba, $^1P\,5f$ is external to the barrier,

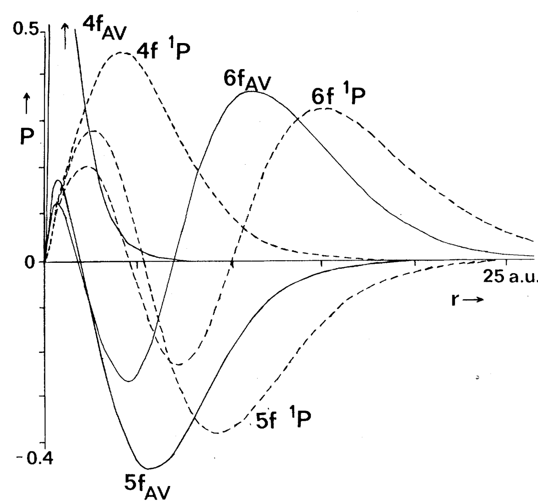

FIG. 1. Wave functions for Ba^{++}.

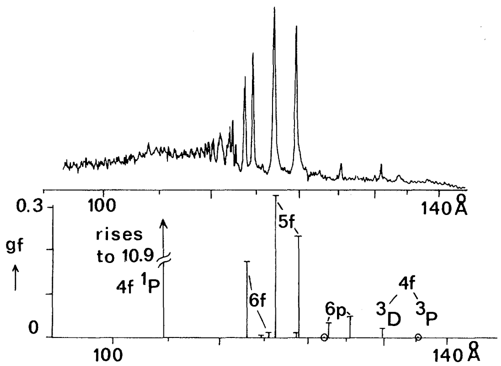

FIG. 2. Comparison between Ba^{++} experimental data (Ref. 1) and Ba^{++} calculation summarized in Table I.

with an amplitude in the inner well lower than that of $5f_{av}$. In Ba^{++}, the situation reverses and $5f\ ^1P$ acquires a significant amplitude in the inner well. Consequently, while the exchange interaction still tends to expel $^1P\ 5f$ to larger r as compared to $5f_{av}$, the spatial overlap between $4d$ and $5f$ actually *increases* for ^1P. The size of the $F^2\ (4d5f)$ integral is a good indicator of $4d$-$5p$ overlap so that the ratio $F_{^1P}{}^2/F_{av}{}^2$ is given for each $4d^95f$ configuration in Table II, where values greater than 1 denote cases in which the $5f\ ^1P$ wave function is enhanced in the core. The enhancement leads to a strengthening of $4d \to 5f$ transitions in Ba^{++} as compared to Ba. Similar effects occur at higher nf, as illustrated by the $4d^96f$ results. It should be noted that the F^2 ratio first exceeds 1 for Ba^{++}. This agrees well with observation[3] which shows that strong discrete structure suddenly appears between Ba^+ and Ba^{++}.

It would seem, although we cannot give a formal proof, that the reversal described above occurs as the $4f\ ^1P$ wave-function collapses, i.e., that it is a property of wave-function collapse of the second kind, after which transitions to nf states $(n > 4)$ become prominent once more.

In conclusion, although our multiconfiguration calculations do not include the term dependence of the hybrid radial wave functions explicitly, they demonstrate that $4d \to nf$ $(n \geq 5)$ transitions (rather than $4d \to np$) must be responsible for the prominent discrete structure below the $4d$ threshold of Ba^{++}. Furthermore, we have identified a physical reason for which an increase occurs in the oscillator strength of $4d \to 5f$ in Ba^{++} as compared to Ba. The behavior of the $4d^9f$ states in Ba^{++} may be described as a second kind of wave-function collapse (collapse in the singlet potential). We do not know of any formalism within which a diagonalization of the full energy matrix in intermediate coupling can be performed taking into account the term dependence of the hybrid wave functions. To a first approximation, however, our calculations for the discrete structure in Ba^{++} should be comparable with experiment, and we therefore show a stick diagram of the calculated spectrum in Fig. 2.

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