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Correlation effects in a relativistic calculation of the $6s^2\,{}^1S_0$—$6s\,6p\;{}^3P_1,{}^1P_1$ transitions in barium

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The energies and oscillator strengths for the spin-allowed $6s^2\,{}^1S_0$—$6s\,6p\;{}^1P_1$ and spin-forbidden $6s^2\,{}^1S_0$—$6s\,6p\;{}^3P_1$ transitions in neutral barium have been determined in relativistic multiconfiguration Dirac-Fock calculations, where restricted relativistic configuration mixing to represent intravalence correlation is combined with a polarization model to account for valence-core electron correlation. The relativistic and correlation effects—as can be seen from this study—are not additive but must be calculated simultaneously. The contributions of different configurations to intravalence correlation in both initial and final states are studied in detail. The present results demonstrate that although inclusion of intravalence correlation considerably decreases the discrepancies between the computed quantities and experimental data, it is nevertheless not sufficient: To achieve good agreement, particularly for oscillator strengths, one must also include core-valence correlation. The core-polarization model used in this study to represent this type of correlation again proves to be quite a satisfactory approximation.

I. INTRODUCTION

The resonance $6s^2\,{}^1S_0$—$6s\,6p\;{}^1P_1$ transition in barium has been the subject of numerous theoretical studies, most of them nonrelativistic. Friedrich and Trefftz[1] included the influence of intravalence correlation on the $6\,{}^1S_0$—$6\,{}^1P_1$ oscillator strength through the configuration-interaction (CI) approach, whereas Kim and Bagus[2] and later McCavert and Trefftz[3] used a multiconfiguration Hartree-Fock (MCHF) scheme to perform this task, but all neglected the core-valence correlation. Although Hameed[4] included the latter effect in an approximate way through a core-polarization correction, he neglected the intravalence correlation and used less accurate Hartree-Fock-Slater (HFS) wave functions. Trefftz[5] later corrected the results of MCHF calculations for the breakdown of LS coupling. Hafner and Schwarz[6] used calculations with empirically adjusted effective-core potentials; intravalence correlation was included through configuration interaction, but the core-valence correlation was limited to a core-polarization correction applied only to the dipole transition operator. Recently Bauschlicher *et al.*[7] employed a relativistic *ab initio* effective-core potential and treated both intravalence and core-valence correlation by the CI approach. The inclusion of relativistic effects in the last two studies allowed for the breakdown of LS coupling and the relativistic contraction and expansion of orbitals.[8] It also permitted computations of the oscillator strength for the spin-forbidden $6\,{}^1S_0$—$6\,{}^3P_1$ transition.

A versatile and powerful tool in atomic structure calculations is the relativistic multiconfiguration Dirac-Fock method (MCDF) which allows for simultaneous optimization of configuration mixing coefficients and relativistic atomic orbitals. Kim and Bagus[2] were the first to use this approach for $6\,{}^1S_0$—$6\,{}^1P_1$ transitions in barium but they restricted themselves to so-called single-manifold[9] calculations which correspond to mixing of relativistic equivalents of a single nonrelativistic configuration, thus allowing only for intermediate coupling. Recently Bruneau[10] performed relativistic MCDF calculations of oscillator strengths for $6s^2\,{}^1S_0$—$6s\,6p\;{}^3P_1,{}^1P_1$ transitions in barium and included intravalence correlation by mixing the relativistic counterparts of $6s^2$, $6p^2$, and $5d^2$ configurations in the ground ${}^1S_0$ state and $6s\,6p$ and $5d\,6p$ configurations in the excited ${}^3P_1,{}^1P_1$ states but neglecting completely the core-valence correlation contribution. He employed the "transition state" concept where the minimization is performed of the sum of total energies of the initial and final states with different weights.[10]

The inclusion of core-valence correlation by mixing configurations within the relativistic MCDF scheme is very complex and tedious, mainly because of three reasons.

(1) In contrast to intravalence correlation, there exist many configurations with roughly equal contributions to be mixed.

(2) The number of relativistic configurations exceeds by many times the number of their nonrelativistic equivalents.

(3) Convergence of the self-consistent field (SCF) process is very difficult and often impossible to achieve for configurations with small contributions which include orbitals with $l \geq 2$.

Consequently, we have previously[11] suggested a practical approach in which most of the intravalence correlation is represented by a modest amount of configuration mixing, and the valence-core correlation is all represented approximately by a core-polarization model. This approach has already proved successful for the $ns^2\,{}^1S_0$—$nsnp\;{}^3P_1,{}^1P_1$ transitions in neutral mercury and cadmium as well as in their isoelectronic sequences.[12,13] In the present study we apply this method to oscillator strength calculations for the spin-allowed $5p^6 6s^2\,{}^1S_0$—

$5p^6 6s\,6p\ {}^1P_1$ and spin-forbidden $5p^6 6s^2\ {}^1S_0 - 5p^6 6s\,6p\ {}^3P_1$ transition in neutral barium. In contrast to Bruneau's[10] calculations, the total energy is minimized separately for all three states involved: ${}^1S_0$, ${}^3P_1$, and ${}^1P_1$, corresponding to what is known as the "optimized level" (OL) scheme.[9] We also study in detail the influence of the various configurations on the oscillator strengths.

II. CALCULATIONS

Four types of relativistic multiconfiguration Dirac-Fock calculations were performed with a version of the computer code by Desclaux[14] in which we have made several modifications. Besides the code added to calculate oscillator strengths and to include core-polarization effects as described below, appropriate modifications were made to the expansion coefficients near the origin, corrections were made to the asymptotic expansion of the wave function and its derivative, and the original predictor-corrector algorithm for solving the one-electron Dirac equation was replaced by a more accurate direct sixth-order algorithm with good stability.

In the first type of calculation (MCDF I), the ground ${}^1S_0$ state is the pure $6s_{1/2}^2$ state, whereas the upper states ${}^3P_1$ and ${}^1P_1$ are described in intermediate coupling;

$$|6\,{}^1S_0\rangle = |6s_{1/2}^2, J=0\rangle \ , \tag{1a}$$

$$\begin{bmatrix} |6\,{}^3P_1\rangle \\ |6\,{}^1P_1\rangle \end{bmatrix} = \begin{bmatrix} b_1 \\ c_1 \end{bmatrix} |6s_{1/2}6p_{1/2}, J=1\rangle + \begin{bmatrix} b_2 \\ c_2 \end{bmatrix} |6s_{1/2}6p_{3/2}, J=1\rangle \ . \tag{1b}$$

The "frozen core" approximation is used with the core orbitals $\ldots 5p^6$ frozen in the ground ${}^1S_0$ state of neutral barium. In the second type of calculation (MCDF II), the description of upper ${}^3P_1, {}^1P_1$ states is unchanged but additional configurations are included in the ground ${}^1S_0$ state:

$$|6\,{}^1S_0\rangle = a_1\,|6s_{1/2}^2, J=0\rangle + a_2\,|6p_{1/2}^2, J=0\rangle + a_3\,|6p_{3/2}^2, J=0\rangle \ . \tag{2}$$

In the third type of calculation (MCDF III) the relativistic equivalents of the $5d\,6p$ configurations are included for the upper ${}^3P_1, {}^1P_1$ states, whereas the ${}^1S_0$ state remains as in MCDF II [Eq. (2)]:

$$\begin{bmatrix} |6\,{}^3P_1\rangle \\ |6\,{}^1P_1\rangle \end{bmatrix} = \begin{bmatrix} b_1 \\ c_1 \end{bmatrix} |6s_{1/2}6p_{1/2}, J=1\rangle + \begin{bmatrix} b_2 \\ c_2 \end{bmatrix} |6s_{1/2}6p_{3/2}, J=1\rangle + \begin{bmatrix} b_3 \\ c_3 \end{bmatrix} |5d_{3/2}6p_{1/2}, J=1\rangle + \left[\begin{array}{c} b_4 \\ \hline c_4 \end{array}\right] |5d_{3/2}6p_{3/2}, J=1\rangle + \begin{bmatrix} b_5 \\ c_5 \end{bmatrix} |5d_{5/2}6p_{3/2}, J=1\rangle \ . \tag{3}$$

Finally, in the fourth type of calculation (MCDF IV) the $5d_{3/2}^2, 5d_{5/2}^2$ configurations are added to the ground ${}^1S_0$ state and the ${}^3P_1, {}^1P_1$ states remain as in MCDF III:

$$|6\,{}^1S_0\rangle = a_1\,|6s_{1/2}^2, J=0\rangle + a_2\,|6p_{1/2}^2, J=0\rangle + a_3\,|6p_{3/2}^2, J=0\rangle + a_4\,|5d_{3/2}^2, J=0\rangle + a_5\,|5d_{5/2}^2, J=0\rangle \ . \tag{4}$$

The valence $6s_{1/2}$, $6p_{1/2,3/2}$, and $5d_{3/2,5/2}$ orbitals are different in the initial and final state and appropriate overlap integrals must be computed in oscillator strength calculations.

First, all four types of multiconfiguration calculations were performed with valence-core correlation entirely neglected, so that one could estimate the influence of intravalence correlation by itself as well as the contribution to the oscillator strengths of different configurations used to describe the initial and final state. Then the fourth type of calculation was repeated with valence-core correlation represented by the core-polarization model (MCDF IV + CP). In this model, the core-polarization potential

$$V_{\mathrm{CP}} = -\tfrac{1}{2}\alpha \left[\sum_i \mathbf{F}_i\right]^2 \tag{5}$$

represents the interaction of the core through its static dipole polarizability α, with the sum of net electric fields $\mathbf{F}_i$ produced in the core by each valence electron at $\mathbf{r}_i$. The expression for the electric field $\mathbf{F}_i = \mathbf{r}_i (r_0^2 + r_i^2)^{-3/2}$ (in a.u.) was chosen to ensure that the interaction remains finite at small r, and the r_0 parameter which appears in $\mathbf{F}_i$ may be considered a measure of the core radius. The one-electron terms of Eq. (5) (the direct core-polarization terms) are included in the one-electron Hamiltonian of each valence electron and the cross or "dielectric" terms are added to the direct Coulomb repulsion term r_{ij}^{-1} between valence electrons.

Oscillator strengths were calculated in the long-wavelength approximation with the dipole-length form of the transition operator and with both experimental and theoretical excitation energies. In versions which include core polarization, the transition matrix element was also corrected by replacing the dipole-moment operator $\mathbf{d} = -\mathbf{r}$ of each valence electron by $\mathbf{d} + \mathbf{d}_c$, where $\mathbf{d}_c = \alpha\mathbf{F}$ is the dipole moment induced in the core by the valence electron. Two versions of MCDF IV + CP calculations are reported which differ by the value of dipole polarizability of the core α. In version CP1 the Hartree-Fock value calculated by Fraga *et al.*[15] for Ba^{2+} ($13.58a_0^3$) was used, whereas in the second version (CP2) the presumably more accurate value ($10.61a_0^3$) computed by Johnson *et al.*[16] in the relativistic random-phase approximation was employed. In both these versions the r_0 parameter was set to the mean radius of the outermost orbital of the unpolarized Ba^{2+} ion ($1.927a_0$). In order to separate the change in oscillator strengths resulting from the modification of valence wave functions (caused by the core-

TABLE I. Percentage composition of states, ionization, and excitation energies; and oscillator strengths computed in the present study for the $6s^2\,{}^1S_0$—$6s\,6p\;{}^3P_1,{}^1P_1$ transitions in neutral barium. For the description of computations, see text.

State					Intravalence correlation				
					+ core polarization				
or	Intravalence correlation only				MCDF II + CP1		MCDF II + CP2		
transition	MCDF I	MCDF II	MCDF III	MCDF IV	*A*	*B*	*A*	*B*	Experiment
				Percentage composition of states					
${}^1S_0 6s^2_{1/2}$	100.00	91.05	91.05	91.83	93.33		93.08		
${}^1S_0 6p^2_{1/2}$		3.43	3.43	2.78	1.79		2.00		
${}^1S_0 6p^2_{3/2}$		5.51	5.51	4.44	2.89		3.21		
${}^1S_0 5d^2_{3/2}$				0.34	0.77		0.65		
${}^1S_0 5d^2_{5/2}$				0.60	1.23		1.06		
${}^3P_1 6s_{1/2}6p_{1/2}$	69.24	69.24	69.09	69.11	71.06		70.54		
${}^3P_1 6s_{1/2}6p_{3/2}$	30.76	30.77	26.07	26.07	24.89		25.25		
${}^3P_1 5d_{3/2}6p_{1/2}$			1.26	1.26	1.22		1.22		
${}^3P_1 5d_{3/2}6p_{3/2}$			2.75	2.74	2.34		2.42		
${}^3P_1 5d_{5/2}6p_{3/2}$			0.83	0.83	0.48		0.56		
${}^1P_1 6s_{1/2}6p_{1/2}$	30.64	30.65	17.68	17.71	14.68		15.51		
${}^1P_1 6s_{1/2}6p_{3/2}$	69.36	69.36	51.85	51.90	50.79		51.08		
${}^1P_1 5d_{3/2}6p_{1/2}$			11.49	11.45	14.05		13.28		
${}^1P_1 5d_{3/2}6p_{3/2}$			1.70	1.70	1.74		1.74		
${}^1P_1 5d_{5/2}6p_{3/2}$			17.29	17.26	18.74		18.40		
				Ionization energies					
${}^1S_0$	0.157 234	0.179 154	0.179 154	0.180 504	0.186 294		0.184 860		0.191 514[a]
${}^3P_1$	0.126 774	0.127 093	0.132 245	0.131 874	0.130 211		0.130 636		0.133 937
${}^1P_1$	0.075 586	0.075 901	0.101 047	0.100 653	0.107 101		0.105 612		0.109 225
				Excitation energies and ${}^1P_1$-${}^3P_1$ splitting					
${}^1S_0$-${}^3P_1$	0.030 460	0.052 061	0.046 909	0.048 630	0.056 083		0.054 224		0.057 577[a]
${}^1S_0$-${}^1P_1$	0.081 648	0.103 253	0.078 107	0.079 851	0.079 193		0.079 248		0.082 289
${}^1P_1$-${}^3P_1$	0.051 188	0.051 192	0.031 198	0.031 221	0.023 110		0.025 024		0.024 712
				Oscillator strengths					
${}^1S_0$-${}^3P_1$ (E)[b]	0.001 79	0.000 448	0.005 90	0.006 40	0.011 07	0.009 16	0.009 60	0.008 32	0.009 94±0.004 97[c]
(T)	0.000 945	0.000 405	0.004 81	0.005 40	0.010 78	0.008 92	0.009 04	0.007 83	
${}^1S_0$-${}^1P_1$ (E)	2.40	1.54	1.80	1.93	1.82	1.55	1.85	1.64	1.59±0.16[d]
(T)	2.38	1.93	1.71	1.87	1.75	1.49	1.78	1.58	1.64±0.16[e]

[a] Reference 17.

[b] Oscillator strengths are calculated with both experimental (E) and theoretical (T) excitation energies.

[c] Reference 18.

[d] Value derived by Hulpke *et al.* (Ref. 19) from their lifetime measurements assuming $f_{{}^1D\text{-}{}^1P}=0.10$.

[e] As in footnote d but $f_{{}^1D\text{-}{}^1P}=0.0034$ as per Bernhardt *et al.* (Ref. 20) (Ref. 7).

polarization potential V_{CP}), from that due to the core-polarization correction to the dipole-moment operator, the computations have been performed with the d_c correction both omitted (A) and included (B). Both excitation and ionization energies have been computed as differences of total energies of the proper systems. The total energy of Ba^+ ion in its ground ${}^2S_{1/2}$ state, used to compute ionization energies, also includes the effect of core polarization on the valence $6s_{1/2}$ electron, calculated with the same α and r_0 parameters as employed for neutral barium. The values of ionization energies for the ${}^1S_0$, ${}^3P_1$, and ${}^1P_1$ states, the ${}^1S_0$-${}^3P_1,{}^1P_1$ excitation energies, the ${}^1P_1$-${}^3P_1$ splitting and the oscillator strengths, computed in the different versions reported here, are presented in Table I and compared with available experimental data.

III. DISCUSSION AND CONCLUSIONS

A. Intravalence correlation

As seen from Table I, the contribution of the $5d\,6p$ configuration is much larger in the ${}^1P_1$ state than in the ${}^3P_1$, and in consequence, the corresponding contribution to ionization energies is roughly five times greater in the ${}^1P_1$ then in the ${}^3P_1$ state. For the ${}^1S_0$ ionization energy, the main improvement comes from the contribution of the $6p^2$ configuration. The two relativistic equivalents of this configuration are also responsible for a major improvement in the ${}^1S_0$-${}^3P_1$ excitation energy, whereas for the ${}^1S_0$-${}^1P_1$ excitation energy and the ${}^1P_1$-${}^3P_1$ splitting, the most important effect is the contribution of the $5d\,6p$ configuration to the upper ${}^3P_1, {}^1P_1$ states. For the ${}^1S_0$-${}^1P_1$ excitation energy, the contributions of the $6p^2$ configuration to the lower state and of the $5d6p$ configuration to the upper one almost cancel each other. Inclusion of the $6d^2$ configuration in the ${}^1S_0$ ground state only marginally changes both ionization and excitation energies as well as the ${}^1P_1$-${}^3P_1$ splitting. The simultaneous inclusion of at least the $6p^2$ configuration in the ground ${}^1S_0$ state and of the $5d6p$ configuration in the excited ${}^3P_1$ state is crucial for the proper order of magnitude of the oscillator strengths for the spin-forbidden ${}^1S_0$-${}^3P_1$ transition. Although the intravalence correlation introduced through inclusion of $6p^2$, $5d^2$, and $5d6p$ configurations within the MCDF scheme greatly improves the calculated ionization and excitation energies, as well as the oscillator strengths, in comparison with those from the intermediate coupling calculations (MCDF I), it is not sufficient to achieve good agreement with experimental data, particularly for the oscillator strengths.

B. Core-valence correlation in the core-polarization approximation

Better agreement with experiment for the ${}^1S_0, {}^1P_1$ ionization energies, the ${}^1S_0$-${}^3P_1$ excitation energy and the ${}^1P_1$-${}^3P_1$ splitting is obtained by including core polarization to account for core-valence correlation. However, the ${}^3P_1$ state and the ${}^1S_0$-${}^1P_1$ excitation energy are rather insensitive to core polarization. This is due to the fact that the "dielectric" term $-\alpha \mathbf{F}_1 \cdot \mathbf{F}_2$ which has negative expectation value for ${}^1P_1$ and positive for ${}^3P_1$ significantly enhances the influence of the direct $-\frac{1}{2}\alpha F_i^2$ polarization term for the ${}^1P_1$ state, whereas for ${}^3P_1$ these two polarization contributions almost cancel each other.[21] For the ${}^1S_0$ state, the dielectric part has a practically negligible effect since here it contributes only to off-diagonal matrix elements, and the whole polarization influence comes from the direct part of $V_{\rm CP}$. The combined enhanced influence of direct and dielectric core-polarization terms on the ${}^1P_1$ state is now comparable to that resulting for the ${}^1S_0$ state from the direct part of $V_{\rm CP}$ (which otherwise would be much larger than its counterpart for ${}^1P_1$) leading in consequence to only a small change in the ${}^1S_0$-${}^1P_1$ excitation energy. The importance of core polarization is even more clearly visible for oscillator strengths, where the best agreement with experiment is achieved when both the $V_{\rm CP}$ potential and the proper correction to the dipole-moment transition operator are included (version B in Table I). As seen from a comparison of MCDF IV + CP1 and CP2 calculations, the 22% decrease in value of α results in a 9.2% (12.2%) decrease in ${}^1S_0$-${}^3P_1$ oscillator strengths and 5.8% (6.0%) increase in ${}^1S_0$-${}^1P_1$ oscillator strengths when calculated with experimental (theoretical) excitation energies. The corresponding change in ionization and excitation energies is less than 3.5% and for the ${}^1P_1$-${}^3P_1$ splitting it is 8.3%. The ${}^1S_0$-${}^1P_1$ oscillator strength computed with the more accurate value[16] of α is in better agreement with experimental data, whereas for the ${}^1S_0$-${}^3P_1$ oscillator strength, the less accurate Hartree-Fock value of α seems to give a better result. However, this better agreement may be fortuitous because of the large experimental error quoted for the spin-forbidden transition. Our "best" MCDF IV + CP2 results, which deviate from experiment by about 16% (21%) for spin-forbidden ${}^1S_0$-${}^3P_1$ transitions and by less than 0.3% (3.7%) for spin-allowed ${}^1S_0$-${}^1P_1$ transition oscillator strengths computed with experimental (theoretical) excitation energies, lie well within the quoted experimental errors of 50% and 10% for the ${}^1S_0$-${}^3P_1$ and ${}^1S_0$-${}^1P_1$ oscillator strengths, respectively.

C. Comparison with other theoretical results

In Table II, our best results (MCDF IV + CP2 B) are compared with other theoretical data. Several conclusions can be drawn from this comparison. The small difference between the nonrelativistic single-configuration Hartree-Fock ${}^1S_0$-${}^1P_1$ oscillator strength of Kim and Bagus[2] and their relativistic Hartree-Fock intermediate coupling result (which corresponds exactly to the result of our MCDF I calculations) demonstrates that the relativistic change in atomic orbitals as well as the breakdown of LS coupling have a small but still important influence on the spin-allowed ${}^1S_0$-${}^1P_1$ oscillator strength. The breakdown of LS coupling is of course crucial for the existence of spin-forbidden ${}^1S_0$-${}^3P_1$ transitions. Inclusion of intravalence correlation in the nonrelativistic MCHF calculations of Kim and Bagus[2] clearly improves the result for the ${}^1S_0$-${}^1P_1$ transition, and as Bauschlicher, Jr. *et al.*[7] noted, if the relativistic and intravalence correlation effects were additive, the combined results of the Kim and Bagus MCHF and DF-IC calculations[2] would be in a good agreement with experiment. The direct evidence that this assumption is not correct and that the correlation effects are coupled, is our MCDF IV results as well as those of Bruneau,[10] where virtually the same configurations as in the MCHF calculations of Kim and Bagus[2] (except for $4f5d$ configuration which makes only a very small contribution[2,10]) where included within the relativistic multiconfiguration Dirac-Fock calculations, yielding a ${}^1S_0$-${}^1P_1$ oscillator strength which is considerably too large in comparison with the experimental data (c.f. Table II). The empirically adjustable relativistic effective-core potential (RECP) results of Hafner and Schwarz[6] are too small for both spin-allowed and spin-forbidden transitions, but, as we pointed out earlier for mercury,[11] their conclusion that core-polarization correction worsens the agreement with experiment for intercombination transitions was premature and a consequence of their neglect of the dielectric part of $V_{\rm CP}$ (the direct one-electron part of $V_{\rm CP}$ may be considered as implicitly included in their calculations through empirical adjustment of the model potential[22]). The *ab initio* relativistic effective core potential technique of Bauschlicher, Jr. *et al.*,[7] which treats both intravalence and core-valence correlation in a configuration interaction (CI) approach, gives results of similar accuracy, when compared with experimental data, as our MCDF IV + CP approach. However, rather high computational effort is required in order to include the valence-core correlation within the CI scheme. The relativistic multiconfiguration Dirac-Fock (MCDF) calculations of Bruneau[10] yield oscillator strengths which are too small for the spin-forbidden and too large for the spin-allowed transition because they

TABLE II. Comparison of our "best" MCDF + CP (MCDF IV + CP2 *B* in Table I) results with other theoretical data and with experiment.

Method of calculation	Excitation energies and $^1P_1$-$^3P_1$ splitting			Oscillator strengths	
	$^1S_0$-$^3P_1$	$^1S_0$-$^1P_1$	$^1P_1$-$^3P_1$	$^1S_0$-$^3P_1$	$^1S_0$-$^1P_1$
HF[a]		0.077			(*E*) 2.64[c] (*T*)
DF-IC[b]		0.081			(*E*) 2.39 (*T*)
MCHF[d]		0.067			(*E*) 1.78 (*T*)
RECP[e]				(*E*) 0.0079 (*T*)	(*E*) 1.48 (*T*)
RECP-MRCV-CI[f]	0.061 880	0.080 720	0.024 226	(*E*) 0.0099 (*T*)	(*E*) 1.70 (*T*)
MCDF[g]	0.047 94	0.078 31	0.030 32	0.003 97	1.912
MCDF + CP[h]	0.054 224	0.079 248	0.025 024	(*E*) 0.008 32 (*T*) 0.007 83	(*E*) 1.64 (*T*) 1.58
Experiment	0.057 577[i]	0.082 289[i]	0.024 712[i]	0.009 94[j] 0.004 97	1.59±0.16[k] 1.64±0.16[l]

[a] Nonrelativistic single-configuration Hartree-Fock result (Ref. 1).

[b] Relativistic Dirac-Fock calculations with allowance for intermediate coupling in the upper state (Ref. 2). These calculations correspond exactly to our MCDF I calculations of Table I.

[c] Oscillator strengths given in this column are computed with experimental (*E*) and/or theoretical (*T*) excitation energies. For some data this information is not available.

[d] Nonrelativistic multiconfiguration Hartree-Fock calculations including intravalence correlation only (Ref. 2).

[e] Empirically adjusted relativistic effective-core potential technique of Hafner and Schwarz (Ref. 6) with intravalence correlation included through configuration interaction (CI) and core-valence correlation accounted for through core-polarization correction but in dipole transition operator only.

[f] *Ab initio* relativistic effective-core potential technique with both intravalence and core-valence correlation treated in configuration interaction (CI) approach (Ref. 7). The entries for the $^1S_0$-$^3P_1$ excitation energy and the $^1P_1$-$^3P_1$ splitting correspond to single-reference configuration core-valence correlation treatment (CV), whereas the remaining results were obtained with its multireference analogue (MRCV) (c.f. Ref. 7).

[g] Multiconfiguration Dirac-Fock calculations of Bruneau (Ref. 10), who employed the "transition state" concept. No core-valence correlation is taken into account. The "best" results of Bruneau (Ref. 10) are quoted here.

[h] Present relativistic multiconfiguration Dirac-Fock results obtained employing the "optimized level" (OL) scheme and treating the core-valence correlation through core-polarization (CP) corrections in one- and two-electron Hamiltonian as well as in the dipole-moment transition operator (version MCDF IV + CP2 *B* of Table I).

[i] Reference 17.

[j] Reference 18.

[k] See footnote d to Table I.

[l] See footnote e to Table I.

entirely neglect the core-valence correlation. This approach corresponds to our MCDF IV calculation, but the "optimized level" scheme, which we adopted, yields an oscillator strength for the spin-forbidden transition which is considerably better than that obtained by Bruneau[10] within the "transition state extended optimized level" scheme. As can be seen from Table II, the inclusion of core-valence correlation in the core-polarization approximation within the relativistic multiconfiguration scheme (MCDF + CP) decisively improves the agreement of MCDF oscillator strengths with experimental data for both the spin-allowed 6^1S_0—6^1P_1 and the spin-forbidden 6^1S_0—6^3P_1 transitions in neutral barium.

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