

# Relativistic and correlation corrections to isotope shift in Ba II and Ba I

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We calculate field and mass shifts for low-lying levels of Ba I and Ba II. Second order many body perturbation theory is used to account for core-valence correlations and valence-valence correlations are included within configuration interaction method. We use the form of the mass shift operator with the first order relativistic correction and compare it with the non-relativistic form, which is usually used for neutral atoms.

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## I. INTRODUCTION

It is known that correlation corrections play an important role in calculations of the isotope shifts (IS) in atoms. Relativistic corrections to IS of the neutral atoms are less studied. In the nonrelativistic approximation the mass shift operator includes the one-electron and two-electron parts, known as the normal mass shift (NMS) and the specific mass shift (SMS) respectively. NMS corresponds to the substitution of the electron mass  $m$  with reduced mass  $\mu = mM_{\text{nuc}}/(m + M_{\text{nuc}})$  and leads to the simple scaling of all atomic energies and transition frequencies. The two-electron SMS term is typically of the same order of magnitude, but is difficult to calculate.

At present many atomic calculations are done within the Dirac-Coulomb, or Dirac-Coulomb-Breit approximations. That means that electronic wave functions are 4-component Dirac bispinors. In such calculations the use of the nonrelativistic mass shift operator seems to be inconsistent. In the quantum mechanical approach the completely relativistic treatment of the mass shift is impossible, but the first order relativistic corrections to the mass shift can be considered relatively easily. The main complication is the following. For the relativistic Hamiltonian the NMS part of the mass shift is no longer accounted for by the reduced mass and does not lead to the general scaling of atomic frequencies. That means that NMS has to be calculated in a similar way to the SMS. In this sense the very division of the mass shift into normal and specific parts is justified only for the nonrelativistic approximation.

According to [1–4] the relativistic corrections to the mass shift scale as  $\alpha Z$ , where  $\alpha$  is the fine structure constant and  $Z$  is the number of protons in the nucleus. That means that relativistic corrections are more important for heavy atoms. On the other hand for heavy atoms the field shift (FS) dominates over the mass shift. That may explain why the latter is usually calculated in nonrelativistic approximation. In this paper we study the role of the relativistic corrections to NMS and SMS terms for the neutral and singly-ionized barium. Here the mass shift is still measurable experimentally, while  $Z = 56$  is sufficiently large to expect noticeable relativistic corrections.

We conclude that even for Barium the nonrelativistic scaling of the NMS term works pretty good. Relativistic corrections to the SMS term are more important. The nonrelativistic operator can still be used, but it should be applied only to the upper component of the Dirac bispinor. Relativistic corrections to this approximation are much smaller than corrections caused by the core-valence correlations.

Barium spectrum is known to be very sensitive to correlation corrections (see, for example, [5–9]). IS calculations for Ba II also demonstrated the important role of correlations [10, 11]. MCHF calculations of FS for Ba II and Ba I were done in [12]. Here we continue these studies. In particular, we calculate correlation corrections to the mass shift in Ba I. We conclude that correlation corrections to SMS are very large. There are also large cancelations between different contributions to SMS. The second order many body perturbation theory (MBPT) overestimates the core-valence correlations both for the energy and for SMS. For the latter the need in the adequate all-order methods is most urgent.

The structure of the paper is as follows. Sec. II gives brief description of our method and the expressions we use for the relativistic corrections to the mass shift. Sec. III presents the results of the calculations and our conclusions follow in Sec. IV. In this paper we use atomic units unless otherwise stated explicitly.

## II. DESCRIPTION OF THE METHOD

### A. CI+MBPT

Here we use the CI+MBPT method suggested in [13]. In this method the configuration interaction (CI) calculation is done for valence electrons using effective Hamiltonian  $H_{\text{eff}}$ . In this paper  $H_{\text{eff}}$  is formed using the second order MBPT. In order to reduce the number of the second order diagrams we use the  $V^{N-2}$  approximation where the core is calculated for the doubly charged ion Ba III. In this case all subtraction diagrams turn to zero [13]. The accuracy of this approximation is not much different from the  $V^{N-1}$  approximation [8, 14, 15].

The second order effective Hamiltonian overestimates core-valence correlations [7, 8]. Without increasing the

amount of necessary calculations the high order corrections can be included with the help of the screening coefficients for the Coulomb interaction in the second order diagrams. We use coefficient 0.7 for the dipole interactions, leaving other multipolarities unscreened.<sup>1</sup>

There are several ways for more accurate treatment of the high order correlation corrections. For example, one can use coupled cluster method [6], or pair equation method [16]. If there is more than one valence electron the latter can be adjusted for the construction of the effective Hamiltonian and followed by the CI for valence electrons [17]. All these methods require much more complicated calculations and are not considered here.

CI+MBPT method is easily reformulated for the IS calculations within the finite-field approximation [18]. In this approximation the IS operator  $H_{\text{IS}}$  is added to the many-particle Hamiltonian  $H$  with an arbitrary coefficient  $\lambda$ :

$$H_\lambda = H + \lambda H_{\text{IS}}. \quad (1)$$

The eigenvalue problem for Hamiltonian (1) is solved for  $+\lambda$  and for  $-\lambda$ . Then, the IS correction to the energy is recovered as:

$$\Delta E_{\text{IS}} = \frac{E_{+\lambda} - E_{-\lambda}}{2\lambda}. \quad (2)$$

All calculations are done independently for the field, normal, and specific parts of the IS. Parameter  $\lambda$  is chosen from the considerations of the numerical stability and smallness of the the non-linear terms. In the CI+MBPT calculations Hamiltonian (1) is used to construct  $H_{\lambda,\text{eff}}$ . That means that  $H_\lambda$  is used on all stages of calculation starting from solving Dirac-Fock equations for atomic core. Because of that we introduced necessary changes to the Dirac-Fock program [19], to the CI code [5], and to our MBPT package.

For Ba II there is only one valence electron above the closed-shell core. In this case CI+MBPT method is equivalent to the Brueckner approximation, where the self-energy correction is added to the Dirac-Fock Hamiltonian. Ba I has two valence electrons and we solve CI matrix equation with the effective Hamiltonian for the two-electron valence space. For the basis set we are using here, the CI space includes about 1000 relativistic configurations of a given parity.

## B. Field shift

The shift for the isotope  $A'$  in respect to the isotope  $A$  is defined as:

$$\Delta E_{\text{IS}}^{A',A} = k_{\text{MS}} \left( \frac{1}{A} - \frac{1}{A'} \right) + k_{\text{FS}} \delta \langle r^2 \rangle^{A',A}, \quad (3)$$

where  $k_{\text{MS}} = k_{\text{NMS}} + k_{\text{SMS}}$  and  $\langle r^2 \rangle$  is the nuclear mean square radius,

$$\delta \langle r^2 \rangle^{A',A} = \langle r^2 \rangle^{A'} - \langle r^2 \rangle^A. \quad (4)$$

In our calculations we use for the nuclear charge distribution the model of uniformly charged sphere of the radius  $r_{\text{nuc}}$ . In this case

$$\langle r^2 \rangle = \frac{3}{5} r_{\text{nuc}}^2, \Rightarrow \delta \langle r^2 \rangle = \frac{6}{5} r_{\text{nuc}} \delta r_{\text{nuc}}, \quad (5)$$

and coefficient  $k_{\text{FS}}$  is given by:

$$k_{\text{FS}} = \frac{5}{6} \frac{\Delta E_{\text{IS}}^{A',A}}{r_{\text{nuc}} \delta r_{\text{nuc}}}. \quad (6)$$

The change of the nuclear potential in the linear in  $\delta r_{\text{nuc}}$  approximation is

$$V_{\text{FS}} = \frac{3Z\delta r_{\text{nuc}}}{2r_{\text{nuc}}^2} \left[ 1 - \left( \frac{r}{r_{\text{nuc}}} \right)^2 \right] \Theta(r_{\text{nuc}} - r). \quad (7)$$

In the calculations of the FS this potential must be substituted in Eq. (1) instead of  $H_{\text{IS}}$ .

FS potential (7) is derived for the uniformly charged sphere. More realistic approximation to the nuclear density is the Fermi distribution. We made test Dirac-Fock calculations for both models and found that for a given nuclear mean square radius the difference for the coefficient  $k_{\text{FS}}$  does not exceed 0.1%.<sup>2</sup>

## C. Mass shift

In the nonrelativistic approximation the mass shift operator has the form [20]:

$$H_{\text{MS}} = H_{\text{NMS}} + H_{\text{SMS}} = \frac{1}{2M} \sum_i \mathbf{p}_i^2 + \frac{1}{M} \sum_{i < k} \mathbf{p}_i \cdot \mathbf{p}_k, \quad (8)$$

Using virial theorem the first sum can be reduced to  $-\frac{m}{M}E$ ,  $E$  being the total energy of the atom. Thus, in the nonrelativistic approximation only the second sum has to be calculated.

According to [4] the relativistic corrections to the mass shift operator in the first order in  $\alpha Z$  require the following substitution in Eq. (8):

$$\mathbf{p} \longrightarrow \mathbf{p} - \frac{\alpha Z}{2r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}}], \quad (9)$$

where  $\boldsymbol{\alpha}$  are Dirac matrices and  $\hat{\mathbf{r}} = \mathbf{r}/r$ . The NMS operator now has the form:

$$H_{\text{NMS}} = \frac{1}{2M} \sum_i \left( \mathbf{p} - \frac{\alpha Z}{2r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}}] \right)_i^2 \quad (10a)$$

$$= \frac{1}{2M} \sum_i \left( \mathbf{p}_i^2 - \frac{\alpha Z}{r_i} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}}]_i \cdot \mathbf{p}_i \right) + O(\alpha^2 Z^2), \quad (10b)$$

<sup>1</sup> Explain about screening coefficients!

<sup>2</sup> Check this number with VK!

where we used the fact that  $[\mathbf{p}, \frac{\alpha Z}{r} (\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}})] = 0$ . For the Dirac equation even the first term in the sum (10b) has to be calculated explicitly, so it may be easier to use the symmetric form (10a).

The relativistic SMS operator:

$$H_{\text{SMS}} = \frac{1}{M} \sum_{i < k} (\mathbf{p} - \frac{\alpha Z}{2r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}])_i \cdot (\mathbf{p} - \frac{\alpha Z}{2r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}])_k, \quad (11)$$

as well as the nonrelativistic SMS operator (8) is similar to the dipole Coulomb interaction. When we add SMS operator to the Hamiltonian we must simply substitute Coulomb two-electron integrals of multipolarity 1 in a following way:

$$R_{ab,cd}^1 \longrightarrow R_{ab,cd}^1 + \frac{1}{M} \mathcal{P}_{a,c} \mathcal{P}_{b,d}. \quad (12)$$

In the nonrelativistic approximation the vertices  $\mathcal{P}_{i,k}$  correspond to the operator  $\mathbf{p}$  and relativistic vertices correspond to operator (9). Note that in relativistic calculations the operator  $\mathbf{p}$  acts on upper and lower components of the Dirac functions. In the nonrelativistic approximation this operator can be applied either to the upper component, or to both components of the Dirac function. Below we compare these two possibilities with more accurate relativistic calculations.

SMS interaction modifies not only two-electron interaction, but also core potential. The following operator has to be added to the exchange part of the self-consistent field:

$$V_{\text{SMS}}|a\rangle = -\frac{1}{M} \sum_{b=1}^{N_{\text{core}}} \mathbf{p}|b\rangle \cdot \langle b|\mathbf{p} - \frac{\alpha Z}{r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}]|a\rangle. \quad (13)$$

In this expression we use asymmetric representation with one nonrelativistic vertex and relativistic correction to another vertex doubled. This representation is particularly convenient for the Dirac-Fock calculations, because the operator part of the potential (13) remains the same as in the nonrelativistic case.

### III. RESULTS OF CALCULATIONS AND COMPARISON WITH THE EXPERIMENT

In this section we present results of calculations for the low-lying levels of Ba II and Ba I. For brevity we skip the results for the energy levels. For Ba I they are somewhat worse than those of the CI+MBPT calculations in the  $V^N$  approximation [7, 8]. For Ba II we present results only for  $s, p$ , and  $d$  electrons. The  $4f$  electrons are known to be extremely sensitive to the correlation corrections. For example, the mean-square radius of  $4f_{5/2}$  orbital changes from 8.9 a.u. in Dirac-Fock approximation to approximately 7.2 a.u. in Brueckner approximation. Technically that means large mixing of the Dirac-Fock

$4f$ -orbital with virtual  $nf$  orbitals. Calculations of the mass shift effects include differentiation of the orbitals and are very sensitive to the quality of the orbitals. Large mixing of the orbitals on a finite basis set may cause unphysical oscillations and lead to low accuracy for such operators as (8).

For Ba I the CI approximation does not reproduce experimental multiplet  ${}^3F_J$  of the configuration  $5d^2$ . Instead of that there are several strongly mixed levels, which can not be uniquely associated with experimental levels. Situation significantly improves when effective Hamiltonian is used. Because of that for the latter multiplet we give only results of the CI+MBPT calculations.

#### A. Field shift

TABLE I: Field shift for Ba II. Columns marked EV and DF correspond to the expectation value and to the Dirac-Fock self-consistent calculation respectively. The column  $H_{\text{eff}}^{(\text{II})}$  accounts for the second order MBPT corrections. Finally, the column  $H_{\text{eff}}^{(\text{sc})}$  corresponds to second order MBPT with screening coefficients. Results of other calculations are given for comparison in the last two columns.

Level	$k_{\text{FS}}$ (GHz/Fm <sup>2</sup> )					
	EV	DF	$H_{\text{eff}}^{(\text{II})}$	$H_{\text{eff}}^{(\text{sc})}$	[11]	[10]
$6s_{1/2}$	3.20	3.41	4.47	4.18	3.89	4.10
$5d_{3/2}$	0.00	-1.10	-1.01	-1.30	-1.22	
$5d_{5/2}$	0.00	-1.03	-0.96	-1.22	-1.15	
$6p_{1/2}$	0.07	-0.12	-0.09	-0.15	-0.15	-0.11
$6p_{3/2}$	0.00	-0.19	-0.18	-0.22	-0.23	-0.24
$7s_{1/2}$	1.05	1.10	1.26	1.22		
$6d_{3/2}$	0.00	-0.23	-0.16	-0.23		
$6d_{5/2}$	0.00	-0.23	-0.17	-0.22		
$7p_{1/2}$	0.02	-0.05	-0.04	-0.05		
$7p_{3/2}$	0.00	-0.07	-0.07	-0.08		

We start IS calculations with the field shift. Tables I and II present results for the coefficient  $k_{\text{FS}}$  in different approximations. First we make calculation in the frozen-core approximation. By this we mean here that potential (7) is not included in the Dirac-Fock equations for the core. For Ba II it simply means calculation of the expectation value of the operator (7) for a given valence orbital. For Ba I this corresponds to the valence CI calculation. Next approximation accounts for the core relaxation in the potential (7). Dirac-Fock equations for the core orbitals now include FS operator, but core-valence correlations are still neglected. This approximation corresponds to the Dirac-Fock calculation of Ba II and CI calculation of Ba I. After that we include core-valence correlations within second order MBPT. Our final calculation includes high order term corrections with the help of the screening coefficient as described above.

We see that core relaxation is particularly important for  $5d$  electrons and MBPT corrections are the largest for  $6s$  electrons. Screening coefficients change the results

TABLE II: Field shift for Ba I. Columns marked as CI(val) and CI correspond to the valence CI calculations. In the former calculation the core is not allowed to relax in the FS potential (7), while in the latter this relaxation is included. Next two columns present results of the calculations with the effective Hamiltonian for valence electrons.

		$k_{\text{FS}}$ (GHz/Fm <sup>2</sup> )			
Level		CI(val)	CI	$H_{\text{eff}}^{(\text{II})}$	$H_{\text{eff}}^{(\text{sc})}$
$6s^2$	$^1S_0$	4.29	4.61	6.51	6.08
$5d6s$	$^3D_1$	1.98	1.46	2.40	1.96
	$^3D_2$	1.98	1.46	2.41	1.99
	$^3D_3$	2.01	1.54	2.48	2.07
$5d^2$	$^1D_2$	1.62	1.03	1.73	1.36
	$^3F_2$			-1.34	-1.75
	$^3F_3$			-1.33	-1.71
	$^3F_4$			-1.30	-1.68
$6s6p$	$^3P_0^o$	2.35	2.35	3.28	3.01
	$^3P_1^o$	2.34	2.33	3.26	2.98
	$^3P_2^o$	2.31	2.29	3.23	2.98
	$^1P_1^o$	2.11	2.03	2.80	2.61
$5d6p$	$^3F_2^o$	0.07	-0.85	-0.87	-1.14
	$^3F_3^o$	0.06	-0.84	-0.87	-1.12
	$^1D_2^o$	0.04	-0.94	-0.92	-1.17
	$^3F_4^o$	0.01	-0.84	-0.88	-1.12

quite noticeably. That indicate that high order MBPT corrections may be large. The difference between pure second order calculations and calculations with screening coefficients can be used as a rough estimate of the high order contributions and of the accuracy of our method. We see that for  $s$  electrons the accuracy is about few percent. For other electrons typical shifts are much smaller and the accuracy is significantly lower.

TABLE III: Comparison with experimental data [11, 12, 21] for FS in optical transitions. All shifts are normalized to the FS in  $^1S_0(6s^2) \rightarrow ^3P_1(6s6p)$  transition in Ba I.

		$k_{\text{FS}}/k_{\text{FS}}(^1S_0(6s^2) - ^3P_1(6s6p))$		
Transition		Exper.	CI	$H_{\text{eff}}^{(\text{sc})}$
Ba I				
$^1S_0(6s^2) - ^1P_1(6s6p)$		1.176	1.132	1.119
$^3D_3(6s5d) - ^1D_2(6p5d)$		1.053	1.088	1.045
$^3D_3(6s5d) - ^3F_3(6p5d)$		1.043	1.044	1.029
$^3D_1(6s5d) - ^1D_2(6p5d)$		1.029	1.053	1.010
Ba II				
$6s_{1/2} - 6p_{1/2}$		1.420	1.548	1.397
$6s_{1/2} - 6p_{3/2}$		1.456	1.579	1.419
$5d_{3/2} - 6p_{1/2}$		-0.365	-0.430	-0.371
$5d_{3/2} - 6p_{3/2}$		-0.337	-0.399	-0.348
$5d_{5/2} - 6p_{3/2}$		-0.332	-0.368	-0.323

In order to compare theoretical FS with the experiment one have to separate FS from the mass shift. For barium isotopes nuclear radii are not known from independent

TABLE IV: Comparison of calculated NMS coefficients with nonrelativistic (NR) values given by Eq. (14). For the convenience we give the ratios of calculated coefficients to the NR ones. NRU corresponds to nonrelativistic NMS operator (8) applied to upper Dirac component; NRB - the same operator applied to both components; R - relativistic operator (10a).

		$k_{\text{NMS}}$ (GHz · amu); $k_{\text{NMS}}/k_{\text{NMS}}^{\text{NR}}$					
Level		DF				$H_{\text{eff}}^{(\text{sc})}$	
		NR	NRU	NRB	R	NR	R
$6s_{1/2}$		1239.0	1.076	1.203	0.992	1342.8	1.003
$5d_{3/2}$		1120.6	0.916	0.841	1.002	1264.6	1.018
$5d_{5/2}$		1112.8	0.907	0.835	1.009	1249.7	1.025
$6p_{1/2}$		941.8	1.053	1.054	0.994	999.7	1.001
$6p_{3/2}$		918.9	0.993	0.992	0.996	970.7	1.004
$7s_{1/2}$		606.1	1.051	1.136	0.994	631.7	0.998
$6d_{3/2}$		547.1	0.971	0.941	0.999	570.7	1.003
$6d_{5/2}$		544.3	0.962	0.933	1.002	567.3	1.007
$7p_{1/2}$		497.3	1.039	1.040	0.995	515.0	0.998
$7p_{3/2}$		488.4	0.995	0.994	0.997	504.7	1.000

measurements<sup>3</sup> and we can only compare relative shifts for different transitions. That can be done with the help of the King plots [23]. In Table III all shifts are normalized to the transition  $^1S_0(6s^2) \rightarrow ^3P_1(6s6p)$  in Ba I. For complicity in Table III we give results of the final calculations with effective Hamiltonian and results of the CI calculations without core-valence correlations.

It is seen that here the difference between two calculations are much smaller than in Tables I and II. Still, the effective Hamiltonian generally slightly improves agreement with the experiment, in particular, for transitions in Ba II.

## B. Mass shift

We start calculations of the mass shift with studying the role of relativistic corrections to NMS. It was pointed out above that as long as we use Dirac equation for electronic wave functions, we can not expect that even nonrelativistic NMS operator (8) leads to the nonrelativistic expression

$$k_{\text{NMS},i} = -3609.5 \times E_i \text{ (GHz} \cdot \text{amu)}. \quad (14)$$

In Tables IV and V we present results of the calculations with nonrelativistic and relativistic NMS operators. Nonrelativistic operator is applied either to upper component, or to both components of the Dirac functions. In the frozen-core approximation we make all three calculations and compare them with Eq. (14). Note that we substitute calculated energies, rather than experimental ones. Because of that Eq. (14) gives different predictions when effective Hamiltonian is used. In the latter case

<sup>3</sup> Check the Ref.[22]!

TABLE V: nonrelativistic NMS coefficients and the ratios of the relativistic and nonrelativistic coefficients for Ba I.

		$k_{\text{NMS}}$ (GHz · amu); $k_{\text{NMS}}/k_{\text{NMS}}^{\text{NR}}$			
Level	CI			$H_{\text{eff}}^{(\text{sc})}$	
$6s^2$	$^1S_0$	1876.4	0.993	2044.7	1.002
$5d6s$	$^3D_1$	1696.2	0.998	1929.3	1.020
	$^3D_2$	1696.3	0.998	1927.0	1.020
	$^3D_3$	1697.1	1.001	1923.0	1.022
$5d^2$	$^1D_2$	1679.9	1.000	1888.4	1.016
	$^3F_2$			1750.3	1.040
	$^3F_3$			1747.2	1.042
	$^3F_4$			1743.1	1.044
$6s6p$	$^3P_0^o$	1714.6	0.993	1822.7	0.976
	$^3P_1^o$	1709.8	0.994	1817.5	0.977
	$^3P_2^o$	1699.2	0.994	1804.8	0.978
	$^1P_1^o$	1603.8	0.995	1747.7	1.004
$5d6p$	$^3F_2^o$	1526.1	0.999	1696.4	1.004
	$^3F_3^o$	1520.4	1.001	1683.4	1.004
	$^1D_2^o$	1512.4	1.002	1684.1	1.010
	$^3F_4^o$	1514.2	1.003	1671.9	1.006

only calculations with relativistic NMS operator (10a) are done. It is seen that final relativistic calculations are rather close to the nonrelativistic expression (14).

It is interesting that application of operator (8) to both components of the Dirac function leads to results which are furthest from nonrelativistic expression and from the final answer. Below we will see that similar conclusion can be made for SMS operator. That means that if the nonrelativistic operator is used, it is better to neglect contribution of the low component of the Dirac function.

In general, calculated NMS for Ba II agrees with Eq. (14) within 1%. For  $5d$  electrons deviation from Eq. (14) reaches 2%. At present we do not know whether this is typical for the electrons with high angular momentum, or the anomaly is caused by the relatively large MBPT corrections to the energy for  $5d$  and  $4f$  electrons. In favor of the former explanation is the fact that deviation is usually larger for the electrons with  $j = l + \frac{1}{2}$ . On the other hand, calculated NMS for  $6d$  electrons are much closer to the nonrelativistic values than those of the  $5d$  electrons. The same applies to core-valence corrections.

For Ba I the difference between calculated NMS and the nonrelativistic prediction (14) is almost constant for all levels of a given configuration. Numerically this difference is close to the sum of the differences for corresponding orbitals in Ba II. Maximal deviation from nonrelativistic prediction is 4% and corresponds to the levels of the configuration  $5d^2$ . For other configurations deviation does not exceed 2%.

Now we consider specific part of the mass shift.<sup>4</sup> We start with Dirac-Fock and CI calculations in the same approximations as were used for NMS. Results of the

TABLE VI: SMS coefficients for Ba II. Notations are the same as in Table IV.

		$k_{\text{SMS}}$ (GHz · amu)			
Level	DF	DF			$H_{\text{eff}}^{(\text{sc})}$
		NRU	NRB	R	R
$6s_{1/2}$		-863.7	-809.4	-920.2	-468.2
$5d_{3/2}$		-1574.5	-1533.1	-1620.2	-1209.7
$5d_{5/2}$		-1568.2	-1530.3	-1633.4	-1235.5
$6p_{1/2}$		-308.6	-329.1	-240.7	-97.3
$6p_{3/2}$		-171.4	-184.4	-175.2	-38.1
$7s_{1/2}$		-236.0	-219.0	-253.6	-94.3
$6d_{3/2}$		-232.7	-226.1	-237.5	-123.1
$6d_{5/2}$		-226.5	-220.3	-239.4	-128.1
$7p_{1/2}$		-121.1	-129.1	-94.7	-36.5
$7p_{3/2}$		-68.1	-73.3	-69.5	-14.7

TABLE VII: SMS coefficients for Ba I.

		$k_{\text{SMS}}$ (GHz · amu)			
Level	CI	CI			$H_{\text{eff}}^{(\text{sc})}$
		NRU	NRB	R	R
$6s^2$	$^1S_0$	-1180.1	-1108.8	-1252.5	-677.2
$5d6s$	$^3D_1$	-1714.6	-1646.2	-1786.9	-1248.4
	$^3D_2$	-1715.2	-1647.7	-1789.1	-1256.9
	$^3D_3$	-1717.4	-1651.1	-1799.1	-1277.0
$5d^2$	$^1D_2$	-1588.1	-1535.5	-1650.5	-1261.8
	$^3F_2$				-1652.6
	$^3F_3$				-1672.2
	$^3F_4$				-1689.0
$6s6p$	$^3P_0^o$	-1019.7	-996.3	-1006.7	-599.1
	$^3P_1^o$	-994.4	-969.4	-997.1	-591.0
	$^3P_2^o$	-931.7	-902.2	-973.3	-578.2
	$^1P_1^o$	-826.8	-792.5	-861.0	-454.7
$5d6p$	$^3F_2^o$	-1473.2	-1453.6	-1463.6	-1169.3
	$^3F_3^o$	-1438.1	-1417.1	-1456.5	-1204.2
	$^1D_2^o$	-1398.7	-1373.1	-1436.1	-1100.7
	$^3F_4^o$	-1399.4	-1376.5	-1447.5	-1176.7

calculations with operators (8) and (11) are given in Tables VI and VII. We see that relativistic corrections here are typically larger than for NMS. The largest relative correction  $\sim 30\%$  takes place for  $np_{1/2}$  levels in Ba II. For other levels relativistic corrections are much smaller. For example, relativistic correction to the SMS coefficient of the ground state of neutral barium is 6%. Note that, again, the application of the nonrelativistic operator only to the upper component of the Dirac function is closer to the relativistic result than the application of the nonrelativistic operator to both components of the Dirac function.

Tables VI and VII also present results of the CI+MBPT calculations. These calculations were done only for the relativistic SMS operator (11). It is clearly seen that MBPT corrections for SMS coefficients are very large. That indicates that second order treatment of the core-valence correlations is not sufficient here. Comparison with the experimental results for several transitions in Ba II and Ba I confirms this conclusion (see

<sup>4</sup> SMS for the level  $^3F_4^o$  must be recalculated!

Table VIII). Clearly, the MBPT correction do not improve the agreement. On the contrary, though of the right sign, they strongly overestimate the core-valence correlation corrections.

TABLE VIII: Calculated and experimental mass shifts for several transitions in Ba II and Ba I. In addition to nonrelativistic and relativistic calculations we also present results of the “conventional” (C) calculation where NMS is taken from Eq. (14) and SMS is calculated with nonrelativistic operator on upper components of the Dirac functions. In the last row we give the absolute average difference between calculations and the experiment.

		$k_{\text{MS}} = k_{\text{NMS}} + k_{\text{SMS}}$ (GHz · amu)				$H_{\text{eff}}$	
Transition		Exper. Ref.[24]	C	CI NRU	R	R	
Ba II							
$6s_{1/2}$	–	$6p_{1/2}$	–277(56)	–222	–174	–350	–35
$5d_{5/2}$	–	$6p_{3/2}$	–1074(9)	–1129	–1237	–1175	–903
Ba I							
$^1S_0(6s^2)$	–	$^3P_1(6s6p)$	–36(9)	22	346	–51	131
$^1S_0(6s^2)$	–	$^1P_1(6s6p)$	–41(9)	–56	19	–101	72
$^3D_3(6s5d)$	–	$^3F_3(6p5d)$	–108(9)	–59	–192	–122	181
$^3D_3(6s5d)$	–	$^1D_2(6p5d)$	–116(19)	–96	–245	–143	70
Average absolute difference:			42	153	48	194	

#### IV. CONCLUSIONS

What conclusions we can make from this work?

1. Calculations of the SMS for the optical spectra of neutral atoms and weakly charged ions can be done with nonrelativistic operator. This operator should be applied only to the upper component of

the Dirac functions. On the same level of accuracy one can use the nonrelativistic scaling for NMS.

2. In the case of Barium the core-valence correlation corrections to SMS are very large. The second order MBPT strongly overestimates these corrections. Significant improvement of the pure valence calculations is possible only with the help of the all-order treatment of the core-valence correlations.
3. Core-valence corrections to the FS are somewhat smaller than for the SMS. The second order MBPT with the screening coefficients accounting for the high order corrections leads to the improvement of the agreement between the theory and the experiment. However, this agreement is much worse than that claimed in [12], where MCDF method was used.

Several questions remain. (i) Since the accuracy of the CI+MBPT calculations appeared to be very poor, we now focus on the valence calculations. Then, one can hardly justify the use of  $V^{N-2}$  approximation. (ii) We claim the important role of the valence correlations. Then we must compare, for example, the full CI and single configuration calculations. (iii) What are our achievements in calculations of FS?

Calculation of IS in Ba II was done by Berengut et al. [11]. One can find several references to the experiment there too (see refs. [15 – 18]). More experimental data for Ba I and II is in [24]. More theory is in [10]. In ref. [21] the  $J$ -dependence of the IS is measured for  $5d \rightarrow 6p$  transition in Ba II. State dependent field isotope shift analysis of the low lying states of Ba I and Ba II was done in [12].

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