Calculations of energy levels and lifetimes of low-lying states of barium and radium

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We use the configuration-interaction method and many-body perturbation theory to perform accurate calculations of energy levels, transition amplitudes, and lifetimes of low-lying states of barium and radium. Calculations for radium are needed for the planning of measurements of parity- and time-invariance-violating effects which are strongly enhanced in this atom. Calculations for barium are used to control the accuracy of the calculations.

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I. INTRODUCTION

Measurements of the effects of parity (P) and time (T) invariance violation in atoms are an effective means to search for new physics beyond the standard model (see, e.g., Ref. [1]). The radium atom is a good candidate for this search due to the sizable enhancement of the P- and T-odd effects arising from the nuclear and electronic structures [2,3]. Preparations for measurements are currently in progress at Argonne National Laboratory [4] and KVI [5].

In our previous work [3] we performed a detailed study of those P- and T-odd effects in radium that are enhanced due to the close proximity of states of opposite parity. Estimates of the lifetimes of all low states of radium were also presented.

A detailed knowledge of the energy levels and transition amplitudes of radium is extremely important at the first stages of the experiment when the trapping and cooling scheme is developed and tested. Energy levels of radium presented in Moore's book [6] are based on works by Rasmussen [7] and Russell [8] conducted as early as 1934. The first work [7] presents measurements of transition frequencies while the second work [8] corrects the interpretation of these measurements. To the best of our knowledge no further measurements have been performed for radium since that time. There is some concern ignited by recent calculations by Bieroń *et al.* [9] that the positions of the energy levels of the $7s6d$ configuration of radium might be lower then those presented in Moore's book [6]. This, if true, can totally destroy the cooling scheme adopted by Ahmad *et al.* [4].

The actual position of the $7s6d\ ^3D_2$ energy level is also important for the enhancement of the P- and T-odd effects considered in Refs. [2,3]. This enhancement is due to the very small energy interval ($\sim 5\ \mathrm{cm}^{-1}$) between states of opposite parity $7s7p\ ^3P_1$ and $7s6d\ ^3D_2$. Any significant change in the position of either state would also destroy the enhancement.

We have not performed accurate calculations of radium energy levels before. However, calculations for barium [10,11], which has a similar electron structure, show that such calculations are possible. The theoretical uncertainty cannot be as low as $5\ \mathrm{cm}^{-1}$ needed to confirm the strong P-odd enhancement due to the small energy interval between states of opposite parity. However, it can be small enough to address any concern about the experimental numbers.

In the present work we perform accurate calculations of the energy levels and $E1$ and $E2$ transition amplitudes for low states of radium and barium. We use the V^{N-2} approximation (see, e.g., Ref. [11]). Relativistic Hartree-Fock calculations are carried out for a doubly ionized ion with both valence electrons removed. The self-consistent potential of the core (the V^{N-2} potential) is used to construct the effective Hamiltonian for the configuration-interaction (CI) treatment of the valence electrons. Core-valence correlations are also included by means of many-body perturbation theory (MBPT). Certain classes of dominating higher-order diagrams for the core-valence correlations are included in all orders in the Coulomb interaction.

The barium and radium atoms have similar electron structure, but more experimental data are available for barium. Parallel calculations for these atoms provide a control of the accuracy. The resulting accuracy for the energies of barium and radium is a fraction of a percent or better for removal energies and for the intervals between ground and low-lying states. There is also very good agreement between experimental and calculated lifetimes of states of barium. This means that the accuracy of the results for radium should also be high.

In the end we see no reason for not trusting the experimental energies of radium presented in Moore's book. Therefore, the trapping and cooling of radium should work as planned.

II. CALCULATIONS

We use the combined configuration-interaction and many-body perturbation theory method (CI+MBPT [12]) and the

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TABLE I. Energy levels of Ba^+ and Ra^+ in different approximations. Energies are given in cm^{-1} with respect to the continuum; minus sign is omitted. $\Delta_c = E(\text{expt.}) - E(\text{HF})$; $\Delta = E(\text{expt.}) - E(\hat{\Sigma}^{(\infty)})$.

State	Expt. [6]	HF	Δ_c	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	Δ
			Ba^+			
$6s_{1/2}$	80687	75339	5348	82318	80816	−129
$5d_{3/2}$	75813	68139	7674	77224	76345	−532
$5d_{5/2}$	75012	67665	7347	76286	75507	−495
$6p_{1/2}$	60425	57265	3160	61180	60603	−178
$6p_{3/2}$	58734	55873	2861	59388	58879	−145
			Ra^+			
$7s_{1/2}$	81842	75898	5944	83826	81988	−146
$6d_{3/2}$	69758	62356	7402	71123	70099	−341
$6d_{5/2}$	68099	61592	6507	69101	68392	−293
$7p_{1/2}$	60491	56878	3613	61386	60702	−211
$7p_{3/2}$	55633	52906	2727	56245	55753	−120

V^{N-2} approximation (see [11]) to perform the calculations. As in the standard CI method, the Schrödinger equation for the wave function of two valence electrons is written in matrix form as

$$(\hat{H}^{\text{eff}} - E)\Psi = 0. \tag{1}$$

Ψ is expressed as an expansion over single-determinant two-electron wave functions

$$\Psi = \sum_i c_i \Phi_i(r_1, r_2). \tag{2}$$

Φ_i are constructed from the single-electron valence basis states calculated in the V^{N-2} potential. E in Eq. (1) is the valence removal energy (energy needed to remove two valence electrons from the atom).

The effective Hamiltonian has the form

$$\hat{H}^{\text{eff}} = \hat{h}_1(r_1) + \hat{h}_1(r_2) + \hat{h}_2(r_1, r_2), \tag{3}$$

where $\hat{h}_1(r_i)$ is the one-electron part of the Hamiltonian

$$\hat{h}_1 = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 - \frac{Z}{r} + V^{N-2} + \hat{\Sigma}_1. \tag{4}$$

$\hat{\Sigma}_1$ is the correlation potential, which represents the correlation interaction of a valence electron with the core. It is essentially the same as for atoms with one valence electron (see, e.g., [11,13,14]).

$\hat{h}_2$ is the two-electron part of the Hamiltonian

$$\hat{h}_2 = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \hat{\Sigma}_2(r_1, r_2), \tag{5}$$

$\hat{\Sigma}_2$ is the two-electron part of the core-valence correlations. It represents screening of the Coulomb interaction between valence electrons by core electrons.

The terms $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ can be calculated using MBPT. The expansion starts from the second order and inclusion of the second-order core-valence correlations into the effective CI Hamiltonian is very important for obtaining good agreement with experiment (see, e.g., [10,12]). However, as demonstrated in Ref. [11], inclusion of higher-order core-valence correlations leads to further significant improvement of the results.

It is convenient to start the calculations from a positive ion (Ba^+ or Ra^+) with one valence electron. The equation for a single-electron valence state v has the form

$$(\hat{h}_1 - \epsilon_v)\psi_v = 0, \tag{6}$$

where $\hat{h}_1$ is given by Eq. (4). Solving this equation produces so-called Brueckner orbitals ψ_v and energies ϵ_v in which correlations with the core are included by means of the correlation potential $\hat{\Sigma}_1$. Comparing ϵ_v with the experimental spectrum of the positive ion is a way to study different approximations for $\hat{\Sigma}_1$. Table I compares energy levels of Ba^+ and Ra^+, calculated in different approximations, with experiment. Hartree-Fock (HF) energies correspond to $\hat{\Sigma}_1 = 0$ in Eq. (6). $\hat{\Sigma}^{(2)}$ is the correlation potential calculated in the second order of MBPT. $\hat{\Sigma}^{(\infty)}$ is the correlation potential in which two classes of higher-order diagrams are included in all orders. These are the *screening of the Coulomb interaction* and the *hole-particle interaction*. This is done in exactly the same way as in our previous work for atoms with one valence electron (see, e.g., [1,14–16]). One can see from the table that inclusion of core-valence correlations is very important for obtaining accurate results and inclusion of higher-order core-valence correlations leads to further significant improvement. The energies obtained with $\hat{\Sigma}^{(\infty)}$ are within 0.2–0.3 % of the experimental values for s and p states, and less accurate for d states.

The column marked Δ_c in Table I lists correlation energies (the difference between Hartree-Fock and experimental energies) of valence states of Ba^+ and Ra^+. One can see that the largest correlation energy is in d states. This means that these

TABLE II. Ground-state ($^1S_0$) removal energies (a.u.) and excitation energies (cm^{-1}) of low states of barium and radium. $\Delta_c = E(\text{expt.}) - E(\text{CI})$; $\Delta = E(\text{expt.}) - E(f_2\hat{\Sigma}_1^{(\infty)})$.

State		Expt. [6]	CI	Δ_c	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	$f_1\hat{\Sigma}_1^{(\infty)}$	$f_2\hat{\Sigma}_1^{(\infty)}$	Δ	Other
					Barium					
$6s^2$	$^1S_0$	−0.55915	−0.52358		−0.56996	−0.55903	−0.55799	−0.55915		
$6s5d$	$^3D_1$	9034	11585	−2551	8956	8425	8730	9040	−6	
	$^3D_2$	9216	11662	−2446	9165	8611	8910	9217	−1	
	$^3D_3$	9597	11835	−2228	9609	8999	9283	9582	14	
	$^1D_2$	11395	12833	−1438	11733	11020	11323	11627	−232	
$6s6p$	$^3P_0$	12266	9947	2319	13088	12377	12400	12270	−4	
	$^3P_1$	12637	10278	2359	13466	12740	12754	12638	−1	
	$^3P_2$	13515	11019	2496	14374	13611	13596	13518	−3	
	$^1P_1$	18060	16919	1141	18631	17778	17832	17834	227	
$5d6p$	$^3F_2$	22065	22018	47	22765	21502	21828	22041	23	
	$^3F_3$	22947	22573	376	23732	22403	22698	22926	21	
	$^3F_4$	23757	23172	585	24624	23230	23500	23746	11	
					Radium					
$7s^2$	$^1S_0$	−0.56690	−0.52546		−0.58071	−0.56687	−0.56567	−0.56695		−0.57979[a]
$7s7p$	$^3P_0$	13078	10380	2698	14202	13277	13293	13132	−53	14268[a]
	$^3P_1$	13999	11240	2759	15118	14161	14166	14027	−28	15159[a]
	$^3P_2$	16689	13473	3216	17879	16813	16764	16711	−22	17937[a]
$7s6d$	$^3D_1$	13716	15231	−1515	14043	13342	13423	13727	−11	14012[a]
	$^3D_2$	13994	15284	−1290	14371	13612	13683	13980	14	14465[a]
										12958[b]
	$^3D_3$	14707	15461	−754	15254	14323	14364	14642	65	15921[a]
	$^1D_2$	17081	16798	283	18052	17007	17060	17333	−252	
$7s7p$	$^1P_1$	20716	18686	2030	21547	20487	20459	20450	266	21663[a]
										20835[b]
$7s8s$	$^3S_1$	26754	24030	2724	27643	26673	26571	26669	85	
$6d7p$	$^3F_2$	28038	26328	1710	29425	27736	27833	28001	37	
	$^3F_3$	30118	27713	2405	31745	29848	29891	30077	41	
	$^3F_4$	32368	29383	2985	34195	32134	32129	32370	−2	

[a]Dzuba *et al.* [17].
[b]Bieroń *et al.* [9].

states are more sensitive to the treatment of the correlations and generally are harder to calculate to high accuracy. This is why the accuracy for d states of Ba^+ and Ra^+ is not as good as for s and p states. Large core-valence correlations for d states also manifest themselves in the energies of two-electron configurations containing d electrons (e.g., $6s5d$ configurations of Ba and $7s6d$ configurations of Ra; see discussion below).

Calculations for positive ions give us a very good approximation for the $\hat{\Sigma}_1$ operator in the Hamiltonian (3) for a two-electron system. However, we also need to calculate the two-electron operator $\hat{\Sigma}_2$. We calculate it in the second order of MBPT. Formally, the MBPT expansion for $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ goes over the same orders of perturbation theory. However, numerical results show that an accurate treatment of $\hat{\Sigma}_1$ is usually more important than that of $\hat{\Sigma}_2$. Although inclusion of the higher-order correlations into $\hat{\Sigma}_2$ may lead to further improvement of the results, we leave this at the moment for future work.

A. Energies of barium and radium

Theoretical and experimental energies of neutral barium and radium are presented in Table II. Experimental values are taken from Moore's tables [6]. We present two-electron removal energies (in a.u.) for the ground state ($^1S_0$) of both atoms. The experimental value is the sum of the ionization potential of the neutral atom and its positive ion. Energies of excited states are given in cm^{-1} with respect to the ground state.

The CI column in Table II corresponds to the standard configuration interaction method [$\hat{\Sigma}_{1,2}=0$ in Eqs. (4) and (5)]. It takes into account correlations between valence electrons but neglects correlations between core and valence electrons. We use B splines to construct the basis of single-

TABLE III. Fitting factors f for rescaling of $\hat{\Sigma}^{(\infty)}$ to reproduce experimental energies of Ba^+, Ba, and Ra^+.

Atom	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
Ba II	0.9777	0.95	0.96	0.94	0.94
Ba I	1.0032	1.046	1.046	0.9164	0.9164
Ra II	0.9777	0.95	0.96	0.96	0.96
Ra I	1.0032	1.046	1.046	0.9359	0.9359

electron states. 50 B splines are calculated in a cavity of radius $40a_B$, where a_B is the Bohr radius. Eigenstates of the Hartree-Fock Hamiltonian are constructed from these B splines and the 14 lowest states above the core in each of the s, $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, $d_{5/2}$, $f_{5/2}$, and $f_{7/2}$ waves are used in the CI calculations. The uncertainty due to incompleteness of the basis is very low. It is $\leqslant 10$ cm^{-1} for s^2 and sp configurations and $\leqslant 50$ cm^{-1} for sd configurations.

The next column (Δ_c) lists the difference between experimental and CI energies. This difference is mostly due to core-valence correlations. There are also contributions to Δ_c due to the Breit interaction, radiative corrections, incompleteness of the basis for valence-valence correlations, etc. However, all these contributions are small.

We include core-valence correlations by introducing operators $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ into the effective CI Hamiltonian [see Eqs. (4) and (5)]. Comparison of the Δ_c values for neutral Ba and Ra presented in Table II with the correlation energies (Δ_c) for positive ions (Table I) reveals that core-valence correlations have a larger effect on the energies of positive ions than on neutral atoms. This is due to a cancellation of contributions from $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$. The Hamiltonian for a positive ion (6) has only $\hat{\Sigma}_1$, while the Hamiltonian for a neutral atom (3)–(5) has both. On the other hand, in the V^{N-2} approximation used in the present work, the $\hat{\Sigma}_1$ operator for a neutral atom is the same as for a positive ion.

The cancellation between the two types of core-valence correlations ($\hat{\Sigma}_1$ and $\hat{\Sigma}_2$) has an effect on the accuracy of the calculations. The accuracy is poorer when the cancellation is stronger. It is easy to see that the strongest cancellation takes place for sd configurations of barium and radium. Indeed, correlation corrections to the energies of d states of Ba^+ and Ra^+ are about two times larger than those for s and p states (see Table I). However, corrections to the energies of sd configurations of neutral barium and radium are about the same as or even smaller than for s^2 and sp configurations.

The column in Table II marked by $\hat{\Sigma}^{(2)}$ lists results obtained with both $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ calculated in the second order of MBPT. We use the same B splines to calculate $\hat{\Sigma}$ as for the CI calculations. However, we use 45 out of 50 eigenfunctions and go up to $l=5$ in the partial wave expansion. Inclusion of second-order $\hat{\Sigma}$ leads to significant improvement of the results. The remaining deviation from experiment is just a small fraction of the total core-valence correction Δ_c. However, we do further steps in trying to improve the results. We replace the second-order $\hat{\Sigma}_1$ with the all-order operator $\hat{\Sigma}_1^{(\infty)}$.

TABLE IV. Reduced $E1$ transition amplitudes (a.u.) for Ba and Ra in different approximations.

Transition		CI	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	Other [3]
			Barium		
$^3P_0$	$^3D_1$	2.6185	2.3149	2.3045	2.3121
$^3P_1$	$^1S_0$	0.3203	0.5281	0.5240	0.4537
$^3P_1$	$^3D_1$	2.2829	2.0104	2.0026	2.0108
$^3P_1$	$^3D_2$	3.8806	3.4309	3.4128	3.4425
$^3P_1$	$^1D_2$	0.2979	0.4675	0.4999	0.1610
$^3P_2$	$^3D_1$	0.5997	0.5262	0.5247	0.5275
$^3P_2$	$^3D_2$	2.2838	2.0012	1.9933	2.024
$^3P_2$	$^3D_3$	5.4285	4.8181	4.7805	4.777
$^3P_2$	$^1D_2$	0.3321	0.3551	0.3402	0.1573
$^1P_1$	$^1S_0$	5.7133	5.4235	5.4695	5.236
$^1P_1$	$^3D_1$	0.0880	0.0850	0.0735	0.1047
$^1P_1$	$^3D_2$	0.5935	0.4143	0.3992	0.4827
$^1P_1$	$^1D_2$	0.9919	1.3062	1.1394	1.047
			Radium		
$^3P_0$	$^3D_1$	3.2996	2.9325	2.9521	3.0449
$^3P_1$	$^1S_0$	0.8241	1.2317	1.2205	1.0337
$^3P_1$	$^3D_1$	2.8836	2.5155	2.5366	2.6389
$^3P_1$	$^3D_2$	4.8393	4.2931	4.3158	4.4399
$^3P_1$	$^1D_2$	0.7095	0.7397	0.8068	0.0467
$^3P_2$	$^3D_1$	0.7799	0.6714	0.6781	0.7166
$^3P_2$	$^3D_2$	2.9438	2.5357	2.5615	2.7283
$^3P_2$	$^3D_3$	6.9465	6.2626	6.2541	6.3728
$^3P_2$	$^1D_2$	0.4285	0.5885	0.5344	0.1499
$^1P_1$	$^1S_0$	5.7703	5.3652	5.4821	5.4797
$^1P_1$	$^3D_1$	0.3736	0.4381	0.4255	0.4441
$^1P_1$	$^3D_2$	0.6162	0.3965	0.3591	1.188
$^1P_1$	$^1D_2$	2.9923	3.3103	3.1379	2.4053

We use the Feynman diagram technique as described in our earlier papers [14–16] to calculate $\hat{\Sigma}_1^{(\infty)}$. The results are presented in column $\hat{\Sigma}_1^{(\infty)}$ of Table II. As one can see, inclusion of higher-order correlations into $\hat{\Sigma}_1$ leads to significant improvement of the removal energies but not of the energy intervals (see also Ref. [11]). There are at least two reasons for this. First, the difference in the $\hat{\Sigma}_1$ operator between the positive ion and neutral atom, and second, higher orders in $\hat{\Sigma}_2$. $\hat{\Sigma}$ is an energy-dependent operator: $\hat{\Sigma} \equiv \hat{\Sigma}(\epsilon)$. It should be calculated at the energy of the state for which it is to be used. For example, $\hat{\Sigma}_s$ for the $6s$ state of Ba^+ should be calculated at $\epsilon = \epsilon(6s)$, etc. Using exactly the same $\hat{\Sigma}_1$ operator for the positive ion and neutral atom corresponds to an approximation in which the energy parameter for $\hat{\Sigma}$ is chosen assuming that the two-electron energy of a neutral atom is equal to the sum of the two single-electron energies of a positive ion. This approximation is too rough and some adjustment in the energy parameter is needed. An accurate adjustment is ambiguous. For example, the s-wave $\hat{\Sigma}$ for the s^2

TABLE V. Lifetimes of low-lying states of barium. Numbers in square brackets denote powers of 10.

	Lower states to decay to				Lifetime				
					Probability (s^{-1})				
State	State	Transition	ω (a.u.)	Amplitude (a.u.)	This work	Ref. [18]	This work	Dzuba *et al.* [3]	Expt.
$^3P_0$	$^3D_1$	$E1$	0.01454	2.305	3.500[5]		2.86 μs	2.83 μs	
$^3P_1$	$^1S_0$	$E1$	0.05758	0.5241	3.743[5]		1.23 μs	1.37 μs	1.345(14) μs[a]
	$^3D_1$	$E1$	0.01642	2.003	1.267[5]				
	$^3D_2$	$E1$	0.01559	3.413	3.150[5]				
	$^1D_2$	$E1$	0.00567	0.4999	3.257[2]				
$^3P_2$	$^3D_1$	$E1$	0.02041	0.5247	1.003[4]		1.44 μs	1.41 μs	
	$^3D_2$	$E1$	0.01958	1.993	1.278[5]				
	$^3D_3$	$E1$	0.01785	4.781	5.570[5]				
	$^1D_2$	$E1$	0.00967	0.3403	4.484[2]				
$^1P_1$	$^1S_0$	$E1$	0.08238	5.470	1.194[8]	1.19(1)[8]	8.35 ns	9.1 ns	8.37(8) ns[b]
	$^3D_1$	$E1$	0.04122	0.0735	2.702[3]	3.1(1)[3]			
	$^3D_2$	$E1$	0.04039	0.3993	7.498[4]	1.1(2)[5]			
	$^1D_2$	$E1$	0.03047	1.139	2.623[5]	2.5(2)[5]			
$^3D_2$	$^1S_0$	$E2$	0.04199	3.125	1.454[−2]		69 s		

[a]Reference [19].
[b]Reference [20].

and *sp* configurations are not the same since these configurations have different energies. Moreover, $\hat{\Sigma}$ operators for different states of the same configuration are not the same since different states have different energies.

In the present paper we use a simpler way of adjusting the value of the $\hat{\Sigma}$ operator, leaving an accurate treatment of its energy dependence for future work. We scale the single-electron part of the operator $\hat{\Sigma}_1$ while leaving the two-electron part $\hat{\Sigma}_2$ unchanged. Numerous tests show that any reasonable change in $\hat{\Sigma}_2$ does not lead to a significant change in the spectra of Ba or Ra. Therefore, we scale $\hat{\Sigma}_1$ to fit known energies of Ba, Ba^+, and Ra^+ and use this scaling to calculate energies of Ra.

The most straightforward way to scale the energy levels of Ra would be to perform an accurate fitting of the energy levels of Ba and use the same scaling parameters to do calculations for Ra. However, this method does not take into account the real difference in electron structure of the atoms. The ordering of the energy levels of Ba and Ra are different. States of the *sd* configuration lie below the *sp* configuration for Ba and above the *sp* configuration for Ra. Actually, there are more similarities between the neutral atom and its positive ion than between neutral Ba and Ra. We can use these similarities to construct a fitting procedure which takes into account the difference between Ba and Ra.

First, we scale $\hat{\Sigma}_1$ to fit the energies of Ba^+ and Ra^+. Fitting coefficients are presented in Table III. They are slightly different for *d* states of Ba^+ and Ra^+ (0.94 for *d* states of Ba^+ and 0.96 *d* states of Ra^+). This is because the 5*d* states of Ba^+ are closer to the core and the correlation correction is larger. Our $\hat{\Sigma}^{(\infty)}$ operator is less accurate for *d* states than for *s* and *p* states and the larger correlation correction leads to a noticeable loss in accuracy. However, with the value of $\hat{\Sigma}_1$ reduced by only six or less percent, energy levels of Ba^+ and Ra^+ are fitted exactly.

Then we use the same scaling of $\hat{\Sigma}_1$ to calculate the energy levels of neutral Ba and Ra. The results are presented in Table II under the $f_1\hat{\Sigma}_1^{(\infty)}$ heading. There are two important things to note. The first is the significant improvement in the agreement with experiment. The second is the remarkable similarity between Ba and Ra which was never this good for any other approximation used so far. Now all ^3D states of both atoms are about 300 cm^{-1} below the experimental values while all ^3P states are about 100–200 cm^{-1} above the experimental values. This is enough to indicate that the experimental energies of Ra are correct or that at least there is no reason to believe otherwise.

However, we do one more step. We change the scaling parameters by fitting to the energy levels of neutral barium. The new values are presented in Table III. This change in the scaling parameters accounts for the energy dependence of the $\hat{\Sigma}_1$ operator discussed above. Then the scaling parameters for Ra are calculated using the formula

$$f_i(\mathrm{Ra}) = f_i(\mathrm{Ba})\frac{f_i(\mathrm{Ra}^+)}{f_i(\mathrm{Ba}^+)}.$$

In other words, barium scaling parameters are corrected using the difference in fitting for Ba^+ and Ra^+. The new fitting parameters for Ra are also presented in Table III.

The results of calculations for Ba and Ra with the new fitting parameters are presented in Table II under the $f_2\hat{\Sigma}_1^{(\infty)}$

TABLE VI. Lifetimes of low-lying states of radium. Numbers in square brackets denote powers of 10.

	Lower states to decay to					Lifetime			
State	State	Transition	ω (a.u.)	Amplitude (a.u.)	Probability (s^{-1})	This work	Dzuba *et al.* [3]	Other calc.	Expt.
$^3D_1$	$^3P_0$	$E1$	0.00291	2.952	1.529[3]	654 μs	617 μs		
$^1D_2$	$^3P_1$	$E1$	0.01404	0.8068	7.722[3]	129 ms	38 ms		
	$^3P_2$	$E1$	0.00179	0.5345	7.973[0]				
$^3P_1$	$^1S_0$	$E1$	0.06378	1.221	2.760[6]	362 ns	505 ns	420 ns,[a] 250 ns[b]	422(20) ns[c]
	$^3D_1$	$E1$	0.00129	2.537	9.850[1]				
	$^3D_2$	$E1$	0.00002	4.316	1.572[−3]				
$^3P_2$	$^3D_1$	$E1$	0.01355	0.6782	4.897[3]	5.55 μs	5.2 μs		
	$^3D_2$	$E1$	0.01228	2.562	5.204[4]				
	$^3D_3$	$E1$	0.00903	6.254	1.234[5]				
$^1P_1$	$^1S_0$	$E1$	0.09439	5.482	1.805[8]	5.53 ns	5.5 ns		
	$^3D_1$	$E1$	0.03189	0.4256	4.195[4]				
	$^3D_2$	$E1$	0.03063	0.3592	2.646[4]				
	$^1D_2$	$E1$	0.01656	3.138	3.194[5]				
$^3D_2$	$^1S_0$	$E2$	0.06376	5.022	3.032[−1]	3.3 s	15 s	4 s[d]	

[a]Reference [21].
[b]Reference [22].
[c]Reference [19].
[d]Reference [9].

heading. One can see that the ^1S, ^3D, and ^3P states of Ba are fitted almost exactly. The ^1D and ^1P states are less accurate because strictly speaking one cannot use the same $\hat{\Sigma}$ for ^3P and ^1P states and for ^3D and ^1D states due to the difference in energies of these states.

Calculations for Ra with the new scaling parameters reduce the deviation of the theoretical values from experiment to about 50 cm^{-1} or less for all low states. Let us stress once more that no knowledge of the Ra spectrum was used to do the fitting. Values of the scaling parameters were found by fitting the spectra of Ba, Ba$^+$, and Ra$^+$. The good agreement of the final numbers with experiment leaves no room for any claim that the experimental values might be incorrect. As discussed by Russell [8], the difference between two possible ways of interpretation of the experimental data is 627.66 cm^{-1}. This is much larger than the difference between our calculated energies and the experimental energies of Ra.

In the last column of Table II we present the results of our previous calculations of energy levels of Ra [17] together with the results of recent calculations for Ra by Bieroń *et al.* [9]. Our previous calculations were very similar to those presented in the table in the $\hat{\Sigma}^{(2)}$ column. They were also obtained in the V^{N-2} approximation with the second-order $\hat{\Sigma}$. However, the basis of single-electron states was different. The difference between the present $\hat{\Sigma}^{(2)}$ results and the results of Ref. [17] can serve as an upper limit on the uncertainty due to incompleteness of the single-electron basis for the valence states. The real uncertainty of the present calculations is several times smaller due to better saturation of the basis.

Calculations of Ref. [9] were performed by means of the multiconfiguration Dirac-Hartree-Fock method. The authors use the results to claim that experimental energies of the $7s6d$ configuration of Ra might be incorrect. Indeed, their calculated value for the $^3D_2$ state is 1034 cm^{-1} below the experimental value. On the other hand, the deviation from experiment of the only other calculated energy level, the energy of the $^1P_1$ state, is only 119 cm^{-1}. No other energy levels of Ra were calculated and no calculations for other two-electron systems were used to control the accuracy. Therefore, it is hard to make any judgement about the quality of these calculations. However, let us remind the reader that calculations for *sd* configurations are more difficult than for *sp* configurations due to the larger correlation interaction of the *d* electron with the core and the stronger cancellation between $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ terms (see discussion above). Therefore, the accuracy obtained for the $^1P_1$ state cannot serve as a guide for the accuracy for the $^3D_2$ state. Apart from that, good agreement with experiment for just one number cannot rule out a fortunate coincidence.

B. Transition amplitudes

The leading contribution to the amplitude of a transition between states v and w of Ba or Ra is given by

$$A_{vw} = \langle \Psi_w | \hat{f} | \Psi_v \rangle, \tag{7}$$

where Ψ_w and Ψ_v are the solutions of Eq. (1) and $\hat{f}$ is the operator of the external field. This expression does not take into account the effect of the external field on the atomic core. This effect, which is known as *core polarization*, is very important and can change the amplitude significantly. It can be included by means of the time-dependent Hartree-

Fock method which is equivalent to the well-known random-phase approximation with exchange (RPA).

Every single-electron core function is presented in the RPA as $\psi_a + \delta\psi_a$, where ψ_a is the Hartree-Fock wave function of the core state a calculated in the V^{N-2} potential; $\delta\psi_a$ is the correction due to the external field. The corrections to all core states are found self-consistently by solving Hartree-Fock-like equations

$$(\hat{H}_0 - \epsilon_a)\delta\psi_a = -\hat{f}\psi_a - \delta V_{core}\psi_a, \tag{8}$$

where H_0 is the Hartree-Fock Hamiltonian, $\hat{f}$ is the operator of the external field, and δV_{core} is the correction to the self-consistent potential of the core due to the effect of the external field. Note that in our case $V_{core} \equiv V^{N-2}$. The δV_{core} term is calculated using the $\delta\psi$ corrections to all core states. The final expression for the transition amplitude has the form

$$A_{vw} = \langle \Psi_w | \hat{f} + \delta V_{core} | \Psi_v \rangle. \tag{9}$$

Calculations are performed in the length gauge.

Amplitudes of electric dipole ($E1$) transitions between low states of barium and radium calculated in different approximations are presented in Table IV. Core polarization is included everywhere since it is known to be an important effect. We study only the effect of core-valence correlations on the amplitude, neglecting valence-valence correlations which we expect to be small and also neglecting structural radiation (external field within the internal lines) and normalization which are known to be small. As with energies, inclusion of core-valence correlations has a significant effect on the amplitudes. On the other hand, amplitudes calculated with $\hat{\Sigma}^{(2)}$ and $\hat{\Sigma}^{(\infty)}$ are not very different.

We also present in Table IV the results of our previous calculations for $E1$ transition amplitudes [3]. In spite of the very simple approximation for the wave functions used in the previous work, the agreement for the amplitudes is generally remarkably good. The exception is the amplitudes that involve a change of spin. These amplitudes are larger in the present calculations than in our previous work. The reason is the underestimation of relativistic effects for the $5d$ state of Ba and $6d$ state of Ra in Ref. [3]. The electric dipole transitions between states of different spin are forbidden in the nonrelativistic limit. Therefore, larger amplitudes mean larger relativistic effects. Since we do not have experimental values for the amplitudes, we can use fine structure intervals instead to see how well relativistic effects are treated in different calculations. One can see from the data given in Table 1 of Ref. [3] that the fine structure intervals between the $^3D_{1,2,3}$ states of Ba and Ra are about two times smaller than the experimental values. In contrast, all fine structure intervals of the present calculations are very close to experiment (see Table II). Therefore, we expect the corresponding amplitudes to be more accurate.

C. Lifetimes of low-lying states of barium and radium

The lifetime of the atomic state i expressed in seconds is given by

$$\tau_i = 2.4189 \times 10^{-17} \Big/ \sum_j T_{ij}, \tag{10}$$

where T_{ij} is the probability of a transition from state i to a lower state j (in atomic units), the numerical factor is to convert atomic units to seconds, and summation goes over all states j that have energies lower than the energy of state i.

In the present paper we consider only electric dipole ($E1$) and dominant electric quadrupole ($E2$) transitions.[1] The probability of the $E1$ transition from state i to a lower state j is (atomic units)

$$T_{ij} = \frac{4}{3}(\alpha\omega_{ij})^3 \frac{A_{ij}^2}{2J_i + 1}, \tag{11}$$

where $\omega_{ij} = \epsilon_i - \epsilon_j$, A_{ij} is the amplitude of the transition (reduced matrix element of the electric dipole operator), J_i is the value of the total angular momentum of the state i, and α is the fine-structure constant. The probability of the $E2$ transition is (atomic units)

$$T_{ij} = \frac{1}{15}(\alpha\omega_{ij})^5 \frac{A_{ij}^2}{2J_i + 1}; \tag{12}$$

here A_{ij} is the electric quadrupole reduced matrix element.

Lifetimes of low-lying states of barium and radium calculated using transition amplitudes from Table IV and experimental energies are presented in Tables V and VI alongside the best available experimental values. For most states there is very good agreement with results of our previous work [3], though there is a significant difference for the $^3P_1$ states of barium and radium and the $^3D_2$ state of radium. This is due to the change in the $E1$ amplitude of the $^3P_1$-$^1S_0$ transition and the $E2$ amplitude of the $^3D_2$-$^1S_0$ transition. We believe that the new values are more accurate due to the better treatment of relativistic effects (see discussion above).

Recently, our attention was brought to the recent experimental work by Scielzo *et al.* [19] in which the transition frequency $^1S_0$-$^3P_1$ in radium was measured and found to be in agreement with Moore's tables [6] and the $^3P_1$ lifetimes for barium and radium were determined (we include the results in Tables V and VI).

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[1] Contributions of $M1$ decays to the lifetimes of states that can decay via $E1$ transitions are beyond the accuracy of the current calculations; estimates show that the contributions of the omitted $M1$ and $E2$ decays to the lifetimes of the metastable states considered are small.

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