Lifetime and hyperfine structure of the $^3D_2$ state of radium

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The energy and lifetime of the metastable $^3D_2$ level of radium play an important role in planned experimental investigations of parity and time reversal violation. The multiconfiguration Dirac-Hartree-Fock (MCDHF) model was employed to compute the oscillator strengths of the $^1P_1$ — $^1S_0$ and $^3D_2$ — $^1S_0$ transitions, and the hyperfine structures of the $^1P_1$ and $^3D_2$ states of radium. The calculations yield the $^3D_2$ lifetime $\tau = 4$ *sec.*

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Parity and time reversal violation effects in atoms are enhanced by various nuclear and atomic mechanisms, and in the last decade several atoms (as well as molecules) were considered as candidates for experimental searches [1]. Recent advances in trapping and spectroscopy of minuscule amounts of atoms make it possible to extend the search into the domain of radioactive elements, of which francium [2] and radium [3] are currently considered the most promising ones. The advantage of radium lies in octupole deformations of nuclei in several isotopes, simple electronic structure $[\mathrm{Kr}]4d^{10}4f^{14}5s^25p^65d^{10}6s^26p^67s^2$, as well as in coincidental proximity of two atomic levels of opposite parity, $7s7p$ $^3P_1$ and $7s6d$ $^3D_2$, which are separated by a very small energy interval 5 cm^{-1}. In the present paper we calculated the energy and the electric quadrupole oscillator strength of the $^3D_2$ — $^1S_0$ transition, the only significant decay channel of the metastable state $^3D_2$. The energy and the electric dipole oscillator strength of the $^1P_1$ — $^1S_0$ 'allowed' transition were calculated for the purpose of calibrating the method and tailoring an appropriate MCDHF model for the $^3D_2$ level, which is the main objective of the present paper. The hyperfine structures of the $^1P_1$ and $^3D_2$ levels were also evaluated, using the same wavefunctions as for the transition rates.

The multiconfiguration Dirac-Hartree-Fock theory [4] has been adopted in the present paper. The wavefunction Ψ for a particular atomic state Γ

$$\Psi(\Gamma PJM) = \sum_r^{NCF} c_r \Phi(\gamma_r PJM) \tag{1}$$

is obtained as the self-consistent solution of Dirac-Fock equation [5] in systematically increased [6, 7] multiconfiguration basis NCF of symmetry-adapted eigenfunctions of J^2, J_z, and parity P. Configuration mixing coefficients c_r are obtained through diagonalization of the Dirac Coulomb Hamiltonian

$$H_{DC} = \sum_i c\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - 1)c^2 - Z/r_i + \sum_{i>j} 1/r_{ij}. \tag{2}$$

All calculations were done with the nucleus modeled as a variable-density sphere, where a two-parameter Fermi function [8]

$$\rho(r) = \frac{\rho_0}{1 + e^{(r-c)/a}} \tag{3}$$

was employed to approximate the charge distribution. The $^{213}_{88}\mathrm{Ra}$ isotope was chosen to set the nuclear electromagnetic parameters.

The configuration expansions were obtained with the active space method in which configuration state functions of a particular parity and symmetry are generated by substitutions from a reference configuration to an active set of orbitals. The active set is then increased systematically until the convergence of the expectation value is obtained. The calculations were divided into two stages. In the first stage, the radial wavefunctions were generated in small multiconfiguration expansions. The spectroscopic orbitals required to form a reference wavefunction were obtained with a minimal configuration expansion, with full relaxation. Then virtual orbitals were generated in five consecutive steps. At each step the virtual set has been extended by one layer of virtual orbitals. A layer is defined as a set of virtual orbitals with different angular symmetries. In the present paper five layers of virtual orbitals of each of the *s,p,d,f,g,h* symmetries were generated. At each step the configuration expansions were limited to single and double substitutions from valence shells to all new orbitals and to all previously generated virtual layers. These were augmented by small subset of dominant single and double substitutions from core and valence shells, with further restriction, that at most one electron may be promoted from core shells (which means, that in the case of a double substitution the second electron must be promoted from a valence shell). All configurations from earlier steps were retained, with all previously generated orbitals fixed, and all new orbitals made orthogonal to others of the same symmetry. The initial shapes of radial orbitals were obtained in Thomas-Fermi potential, and then driven to convergence with the self-consistency threshold set to 10^{-8}. All radial orbitals were separately optimized for each of the three states of interest, i.e. $^1\mathrm{S}_0$, $^1\mathrm{P}_1$, $^3\mathrm{D}_2$.

In the second stage, the configuration-interaction calculations (i.e. with no changes to the radial wavefunctions) were performed, with multiconfiguration expansions tailored in such a way, as to capture the dominant electron correlation contributions to the expectation values. The valence and core-valence effects constitute the dominant electron correlation contributions in the oscillator strength calculations [9], therefore all single and double substitutions were allowed from several core shells and both valence shells (i.e. $7s^2$, $7s7p$, or $7s6d$, depending on the state) to all virtual shells, with the same restriction as above, i.e. that at most one electron may be promoted from core shells. The virtual set was systematically increased from one to five layers. In a similar manner, several core shells were systematically opened for electron substitutions — from the outermost $6p$ to $5s5p5d6s6p$ shells. The effects of substitutions from $4s4p4d4f$ shells were estimated separately and turned out to be below 1 percent in the case of hyperfine structures, and a fraction of a percent in the case of transition rates. The transition rates were calculated with the biorthonormal technique [10, 11], which permits the application of standard Racah algebra, while retaining the advantage of wavefunctions separately optimized for each state. The Optimal Level form of the variational expression [8] was applied in all variational calculations.

Figure 1 presents the weighted oscillator strength of the $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ transition as a function of the size of the virtual orbital set, in the 'core-valence' approximation described above. The transition rates were calculated in Babushkin and Coulomb gauges, which in the non-relativistic formulation correspond to length and velocity form of the transition integral, respectively. The points labeled 'experimental energy' refer to the 'scaled' oscillator strength, i. e. the value obtained with the experimental ($20715.71\mathrm{cm}^{-1}$) transition energy. As can be seen in the Figure 1 and in the first three columns of the Table I, the energy, as well as oscillator strength for the $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ transition converge within five layers of virtual orbitals. The close encounter of all four curves at $n = 8$ is also worth noting, as an illustration of an accidental coincidence which might be inadvertently and prematurely taken as a 'final' result.

The core-core correlation effects were estimated in three separate configuration-interaction calculations. In the first, double substitutions from the core $6p$ shell to one layer of virtual orbitals were added to the largest

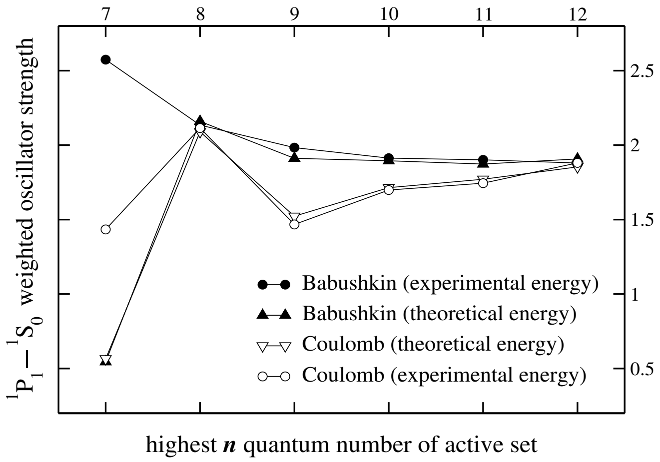

FIG. 1: Oscillator strength of the $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ transition in Babushkin and Coulomb gauges, as a function of the highest principal quantum number of the virtual orbitals; core-valence approximation — see text for details

core-valence expansion. In the second, double substitutions were extended on the $6sp$ shells and again supplemented with the largest core-valence expansion. In the third, double substitutions from the core $6sp$ shells to five layers of virtual orbitals were added to the largest core-valence expansion. The results of these calculations are presented as 'core-valence+core-core' entries in Table I. It should be noted that these results should be treated only as a very crude estimate. The $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ transition energy calculated in the 'core-valence+core-core' approximations indicates that there are significant core-core effects on energy which are not accounted for in our simple core-core correlation model. The Breit and QED corrections were estimated with the step-wise procedure described in [6], terminated in a relatively small-scale configuration-interaction calculation where multiconfiguration expansions were limited to core-valence substitutions from the valence shells and the core $6p$ shell to one layer of virtual orbitals. The matrix elements of the Breit operator in low-frequency limit

$$B_{ij} = -\frac{1}{2r_{ij}}\left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r_{ij}})(\boldsymbol{\alpha}_j \cdot \boldsymbol{r_{ij}})}{r_{ij}^2}\right] \qquad (4)$$

were evaluated perturbatively, as described in [15]. The QED effects included vacuum polarisation and self-energy [16], the latter limited to diagonal matrix elements and therefore not affecting energy-scaled transition rates.

Magnetic dipole hyperfine structure constant A of the $^1\mathrm{P}_1$ state was also calculated, as an additional test of saturation of the multiconfiguration expansions. The calculated value of A is compared in Table I with experimental result [13] and with the value of Dzuba *et al*, obtained in the RHF+CI+RPA approximation [14]. Our final value of A lies within 0.5% from experimental result, but it should be noted that agreement this close is very likely

TABLE I: Calculated transitions energies [cm^{-1}] and weighted oscillator strengths of $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ and $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transitions, and magnetic dipole hyperfine structure constants A [MHz] of $^1\mathrm{P}_1$ and $^3\mathrm{D}_2$ states of $^{213}_{88}\mathrm{Ra}$ ($\mu_N = 0.613\ nm$). (B) — Babushkin gauge; (C) — Coulomb gauge; DF — uncorrelated Dirac-Fock; core-valence — ($5spd6sp \rightarrow 5$ virtual layers); core-core(6p-1v) — ($6p \rightarrow 1$ virtual layer); core-core(6sp-1v) — ($6sp \rightarrow 1$ virtual layer); core-core(6sp-5v) — ($6sp \rightarrow 5$ virtual layers). All oscillator strength values and corrections are energy-scaled, except 'non-scaled core-valence', as indicated in the second row. The values of the oscillator strength of the $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transition are multiplied by 10^9.

	$^1\mathrm{P}_1$ — $^1\mathrm{S}_0$			$^3\mathrm{D}_2$ — $^1\mathrm{S}_0$			hfs A	
	Energy	Oscillator strength		Energy	Oscillator strength			
		gf(B)	gf(C)		gf(B) [10^{-9}]	gf(C)	$^1\mathrm{P}_1$	$^3\mathrm{D}_2$
DF	15191	2.574	1.434	11698	0.185	0.015	−1105	1489
non-scaled core-valence	21019	1.907	1.854	11518	5.388	5.136	−2470	2941
scaled core-valence		1.880	1.881		9.663	6.240		
core-valence + core-core(6p-1v)	24756	1.967	1.857	13005	8.957	5.794	−2390	2829
core-valence + core-core(6sp-1v)	25438	1.979	1.850	13091	8.871	5.731	−2388	2791
core-valence + core-core(6sp-5v)	21094	2.438	1.984					
Breit correction	8	0.001	−0.015	−81	−0.218	−0.136	55	−53
QED correction	−267	0.027	−0.015	−52	0.1	0.1	27	285
total	20835	2.466	1.954	12958	8.753	5.695	−2306	3023
experiment [12, 13]	20716			13994			−2314.8±2.5	
RHF+CI+RPA [14]	21033	1.906[a]		14042	2.552[a]		−1648	1749

[a]Calculated from the lifetimes published by Dzuba *et al* [14].

accidental, because our core-valence expansions were not saturated enough to fully converge the hyperfine expectation values, the virtual set was not optimised for hyperfine interaction calculations, and the value of the nuclear magnetic dipole moment, $\mu_N = 0.613\ nm$, is limited to 3 significant digits [17, 18].

The calculations for the $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transition were performed in a similar manner to those of $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ transition. Figure 2 presents the weighted $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ oscillator strength as a function of the size of the virtual orbital set, in the 'core-valence' approximation described above. Together with the data presented in Table I, they indicate that oscillator strengths of the $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transition, calculated in systematically enlarged core-valence approximations in Babushkin and Coulomb gauges, converge when the transition energy is about 2500 cm^{-1} smaller than the value reported by Moore [12]. It would be tempting to conclude, that the excitation energy of the $^3\mathrm{D}_2$ state of radium should be remeasured or reanalized. If the experience from light atoms is any guide, in sufficiently saturated and properly converged calculations core-core correlation effects usually yield a relatively small correction to the calculated transition rates, compared to valence and core-valence correlation effects [19] (and compared to core-core correlation effect on total energy). However, accurate MCDHF calculations of spectroscopic properties of heavy neutral atoms are still a largely uncharted territory [20] (in fact, large core-core correlation effects on transition energies and rates had indeed been observed in elements Lr and Lu [21]). The core-core model adopted for the $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transition is limited to single and double substitutions from $6sp$ electron shells to one layer of virtual shells. These should

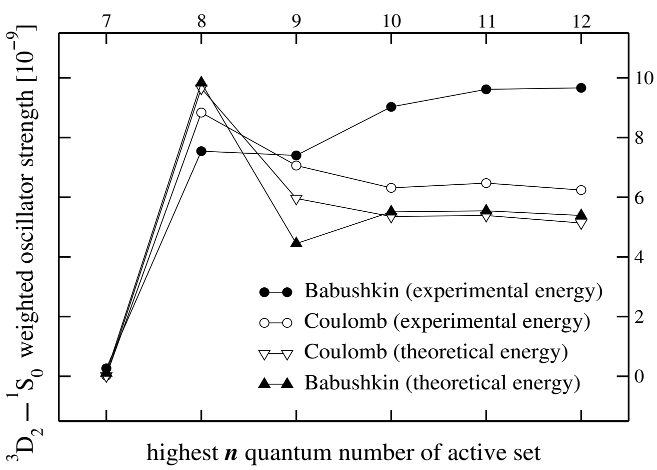

FIG. 2: Oscillator strength of the $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transition in Babushkin and Coulomb gauges, as a function of the highest principal quantum number of the virtual orbitals; core-valence approximation — see text for details

capture the large part of core-core correlation effects, but certainly do not warrant saturation and may cause significant imbalance in energy between the states. When a similar set of virtual orbitals is used for both the ground and the excited state of a transition, the ground state is often less well correlated, yielding smaller excitation energy. This is evident from poor values of transition energy in our 'core-valence+core-core' models. The effect of core-core substitutions on transition rates is of the order of 30% in the case of $^1\mathrm{P}_1$ — $^1\mathrm{S}_0$ transition, and 9% in the case of $^3\mathrm{D}_2$ — $^1\mathrm{S}_0$ transition, but for the latter more restricted core-core model was adopted. Gauge agreement for electric quadrupole transition is computationally a more difficult problem than for electric dipole, but the computer limitations did make it practical not to extend the calculations of core-core effects on the $^3D_2$ — $^1S_0$ transition. In fact, the proper treatment of core-core effects would involve a systematic study of the effects introduced by single, double, triple, and quadruple substitutions from several core shells to a sufficiently saturated set of virtual orbitals, as described in [7]. In the case of $^3D_2$ — $^1S_0$ transition in radium double substitutions alone would generate multiconfiguration expansions in excess of two million configurations, which is about an order of magnitude more than the capacity of computer systems at our disposal. Further discussion and possible refinement of the present calculations should therefore be postponed for at least three full cycles of Moore's law [22], and preferably until experimental verification of the $^3D_2$ — $^1S_0$ transition energy. The Breit correction was estimated with the procedure analogous to the one used for the $^1P_1$ — $^1S_0$ transition. The (relative) size of the QED correction is expected to be of the same order as in the case of $^1P_1$ — $^1S_0$ transition. The overall effect of the QED correction is to increase the $^3D_2$ — $^1S_0$ transition rate, as expected from a simple semi-analytical analysis. Based on the data presented in Table I, we estimate the lifetime of the $^3D_2$ state $\tau = 4$ *sec*, which is about four times smaller than 15 *sec* predicted by Dzuba *et al* [14]. The structure of the virtual set generated for all three states of interest indicates that the values obtained in Babushkin gauge are better saturated than corresponding values in Coulomb gauge. The latter are usually more sensitive to core-core correlation effects [23] and exhibit more oscillatory behavior with respect to the size of the virtual set [24]. Therefore the Babushkin oscillator strength in the core-valence approximation served as the primary source of the calculated lifetime of the $^3D_2$ state. The core-core results should rather be treated as indications of accuracy of the calculations, together with the values obtained in the Coulomb gauge (with the usual caution that gauge difference is only a lower limit of the accuracy). The electric quadrupole oscillator strength in Babushkin gauge scales with the fifth power of the transition energy, therefore the 'non-scaled' lifetime (i.e. obtained with the theoretical value of the transition energy in 'core-valence' approximation) is 50% larger than the 'energy-scaled' result. Our fully ab-initio value of lifetime, vindicated by the close agreement between the results obtained in the two gauges, is $\tau = 6$ *sec*. An experimental verification of the transition energy will be necessary to resolve the discrepancy.

The $^3D_2$ state has two more decay channels — to the $^3P_0$ and $^3D_1$ states. However, small-size calculations indicate that the rates of both transitions are several orders of magnitude smaller than $^3D_2$ — $^1S_0$ rate and therefore do not contribute appreciably to the $^3D_2$ lifetime. Similar reasoning applies to the $^1P_1$ decay rate.

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