

# The low-lying level structure of atomic lawrencium ( $Z = 103$ ): energies and absorption rates

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**Abstract.** The low-lying level structure of atomic lawrencium has been calculated by using medium- to large-scale multiconfiguration Dirac-Fock wave functions. From these computations, an overview on the excitation energies and absorption rates is compiled for the 30 lowest levels of the neutral atom with regard to its  $7s^27p^2P_{1/2}^{\circ}$  ground state. For many of these levels, an accuracy of  $\sim 1200\text{ cm}^{-1}$  is estimated by performing analogue computations for the homologous element lutetium. From the predicted level scheme, the excitation energies of about 15 levels fall into the spectroscopically relevant region between 20 000 and 30 000  $\text{cm}^{-1}$  and, hence, might help in the set-up and interpretation of forthcoming experiments on the resonant excitation of atomic Lr.

**PACS.** 31.25.-v Electron correlation calculations for atoms and molecules – 32.70.Cs Oscillator strengths, lifetimes, transition moments

## 1 Introduction

Spectroscopic investigations on the super-heavy elements (SHE) are of fundamental interest in understanding the nuclear, atomic and chemical properties of isotopes near to the border of the nuclear chart. Many of these case studies on the trans-einsteinium elements are initiated and performed with the hope, that they might help in predicting the properties of yet undiscovered isotopes and as a guide to researchers for designing new experiments. In practice, however, the atomic spectroscopy of SHE with charge numbers  $Z \gtrsim 100$  has remained a challenge because these elements have all to be produced in nuclear fusion reactions with rates of sometimes only a few atoms per week [1]. From the transuranium elements ( $Z > 92$ ), in fact, only neptunium and plutonium have been found in nature and these only in trace amounts [2]. Therefore, the synthesis of SHE through nuclear reactions has become a very important source for understanding the behaviour of matter under extreme conditions. In addition, the study of SHE is of great theoretical interest also since the relativistic effects become so important for these atoms and ions, that the simple extrapolation of trends from the periodic table of elements, such as for the ionization potentials (IP), electron affinities or the formation of chemical complexes does no longer result in reliable predictions.

Up to the present, the most advanced method for studying the trans-einsteinium elements is the aqueous phase [3] and gas phase chemistry at single atoms [4]. Using these techniques, detailed chemical information have been provided already for all elements up to the nuclear charge number  $Z = 108$  [5]. In nuclear chemistry, one of the first goals of these experiments is often to compare the (chemical) properties within a group of homologous elements, i.e. along the ‘columns’ of the periodic table. In atomic spectroscopy, in contrast, the Resonance Ionization Spectroscopy (RIS) has been found a powerful technique and was shown sensitive enough to be applied to radioactive nuclei with short half-lives ( $>1\text{ ms}$ ) as well as for very low production rates [6]. The power of this technique has been demonstrated not only in the hyperfine spectroscopy of  $^{240f,242f,244f}\text{Am}$  fission isomers [7,8] but also in the successful level search of a few low-lying levels of atomic fermium [9,10]. In these measurements, neutral fermium in a buffer gas cell was first excited by one laser beam into a resonant (odd-parity) level *before* the atoms were ionized by means of a second laser. Based on detailed computations of several resonances, and including the analysis of the absorption rates, two fermium resonances at  $25\,099.8\text{ cm}^{-1}$  and  $25\,111.8\text{ cm}^{-1}$  could be identified experimentally and have raised the hope that such low-lying resonances will be observed also for other heavy elements in the near future [9,11]. In fact, these

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experiments demonstrated the great advantage of the RIS techniques which can be applied even, if the number of atoms is really low and if no experimental information on the level scheme is available.

From the viewpoint of atomic spectroscopy on SHE, nobelium and lawrencium are currently the two most prominent candidates. For nobelium, in fact, a first experiment is presently prepared at the GSI in Darmstadt in order to determine some of the low-lying resonances between 20 000 and 30 000  $\text{cm}^{-1}$  [12]. In these *on-line* measurements, the isotope  $^{254}\text{No}$  will be produced at the GSI UNILAC by the reaction  $^{208}\text{Pb}(^{48}\text{Ca}, 2n)^{254}\text{No}$  with rather a large cross section  $\sigma = (3.4 \pm 0.4)$  b and separated by the SHIP from the  $^{48}\text{Ca}$  projectiles beam. Indeed, the  $5f^{14}7s^2$  ground configuration of nobelium renders this element an ideal candidate to test the predictions from various theoretical (semi-empirical and *ab initio*) approaches; this closed-shell ground configuration, in particular, may facilitate also the determination of the IP, leaving the ion within a stable  $5f^{14}7s^2\text{S}_{1/2}$  level [13,14]. Furthermore, the present limit in the search for unknown atomic levels may be reached for the heaviest actinide, i.e. for lawrencium ( $Z = 103$ ), for which the isotope  $^{255}\text{Lr}$  ( $t_{1/2} = 21.5$  s) can be produced via the reaction  $^{209}\text{Bi}(^{48}\text{Ca}, 2n)^{255}\text{No}$  with a cross section of  $0.3 \mu\text{b}$  [15]. However, since nobelium (and all the elements beyond) have to be produced *on-line* in nuclear collisions, the success of such experiments depends critically on the quality of the level predictions, on which the search for new lines is built. Beside of the excitation energies, hereby the absorption rates are of immediate importance also because these rates decides eventually about the ‘efficiency’ with which the levels can be excited from the ground state of the atoms (or ions) by using RIS techniques.

In this contribution, we report about a relativistic multiconfiguration Dirac-Fock (MCDF) study on the low-lying level structure of atomic lawrencium for which a  $5f^{14}7s^27p^2\text{P}_{1/2}^\circ$  ground state were predicted and confirmed by several extensive computations during recent years [16–18]. Since the  $6d$ ,  $7s$  and  $7p$  (one-electron) energies are nearly degenerate for most of the heaviest actinides, lawrencium exhibits already a rather elaborate level structure due to the  $6d7s^2$ ,  $6d^27s$ ,  $7s^27p$  and  $6d7s7p$  configurations. Until now, however, only the first few excitation energies between the  $5f^{14}7s^27p^2\text{P}_{1/2}^\circ$  ground state and the  $6d7s^2^2\text{D}_{3/2}$  and  $^2\text{D}_{5/2}$  levels have been considered in detail by using semi-empirical [16,19] as well as large-scale MCDF [18] and relativistic coupled-cluster (RCC) computations [17]. For spectroscopic investigations, instead, the energy region between 20 000 and 30 000  $\text{cm}^{-1}$  is of predominant interest due to the available (tunable) laser systems and the request of efficiency, namely, that the atoms need to be ionized already by the second photon. Apart from predicting the level energies in this *optical* region above, therefore, the E1 absorption rates from the  $^2\text{P}_{1/2}^\circ$  ground state into the (even-parity) excited levels is required in order to focus in these measurements on sufficiently strong resonances.

In the next section, we briefly summarize the MCDF method and how it has been utilized below in order to generate wave functions of sufficient detail. Computations have been carried out for the 30 lowest odd- and even-parity levels of lawrencium with total angular momenta  $J = 1/2, \dots, 9/2$ , by using medium- to large-scale wave function expansions. The excitation energies and absorption rates with respect to the  $5f^{14}7s^27p^2\text{P}_{1/2}^\circ$  ground level are presented and discussed in Section 3. From an analogue computation of the homologous element lutetium ( $Z = 71$ ), our theoretical excitation energies are estimated to be accurate within either 1200  $\text{cm}^{-1}$  or 2400  $\text{cm}^{-1}$  (for two different groups of levels), apart from a few other levels for which no experimental information is available (for lutetium) or which appeared sensitive to the wave function expansion. Moreover, comparison is made with previous computations as available from the literature. Finally, a short outlook is given on a few possible and desirable experimental investigations.

## 2 Theory and computations

In calculating the level structure of SHE, one often faces difficulties which do either not occur for low- and medium- $Z$  elements or are much less pronounced in that case. Beside of (i) strong relativistic and quantum electrodynamical (QED) effects, which cannot be treated yet in full detail for the heavy elements [20]; (ii) the low-lying level structure of most of these elements is determined by a number of overlapping and nearly degenerate configurations. This ‘overlap’ becomes particularly pronounced for the lanthanides and actinides with their open  $nf$ -shells ( $n = 4, 5$ ), but occurs also for other elements with a nominal rather simple ground configuration, such as the  $7s^27p$  configuration of atomic lawrencium; in addition, further complexity arises (iii) from the large *number of electrons* which have to be treated explicitly in any *ab initio* theory in order to explain the low-lying spectra of such elements. These difficulties enforces one to go up to the limits of what is computational feasible at the time given. Today, there are mainly two *ab initio* methods available for studying the electronic structure of (nearly neutral) SHE: The MCDF and the relativistic coupled-cluster (RCC) method which were found both useful to provide accurate results. While the coupled-cluster technique allows rather easily the self-consistent incorporation of the Breit interaction, that is a computational feature which has not been fully realized in all the MCDF codes, most RCC calculation were restricted to rather simple shell structures (with not more than two electrons or holes outside of closed shells otherwise). The MCDF method, in contrast, is known to be flexible with regard to the shell structure and the computation of — quite different types of — excitation and decay rates but often suffers on the *size* of the wave function expansions which need to be treated explicitly. In the coupled-cluster approach, in addition, some omitted correlation contributions can be taken into account also by means of low-order many-body diagrams [21], an

advantage which cannot be utilized so easily with MCDF wave functions.

In our computations below, the wave functions have been generated by means of the widely-used atomic structure package GRASP92 [22], which is an implementation of the MCDF method. Since the basic concepts and features of this method has been presented at various places elsewhere [23,24], here we shall give only a brief account on the theory. In the MCDF method, an atomic state is approximated by a superposition of configuration state functions (CSF) of the same symmetry,

$$\psi_{\alpha}(PJM) = \sum_{r=1}^{n_c} c_r(\alpha) |\gamma_r PJM\rangle, \quad (1)$$

and is optimized usually on the basis of the (many-electron) Dirac-Coulomb Hamiltonian,  $H_{DC}$  [22]. The CSF are constructed from a product of single electron wave functions through a proper coupling of the angular momenta of the individual subshells and the antisymmetrization of the basis states. The mixing coefficients  $\{c_r(\alpha)\}$  and radial orbitals are then optimized simultaneously, based on the expectation values  $\langle \psi_{\alpha} | H_{DC} | \psi_{\alpha} \rangle$  of one or several atomic states. The finite nucleus effects are taken into account by assuming an extended Fermi distribution for the nucleus. Using the orbitals from the optimization procedure above, a configuration interaction calculation may be performed in addition in order to include the dominant QED effects and the relativistic corrections to the electron-electron interaction by diagonalizing the Dirac-Coulomb-Breit Hamiltonian matrix.

Typically, the major distinction between different MCDF computations arises from the number of CSF,  $n_c$ , in equation (1) which are taken into account and which, to a certain extent, reflects the amount of electron correlations incorporated into the calculations. Wave function expansions (1) of several ten or even hundred thousand CSF can nowadays be applied with the hope of obtaining a sufficiently accurate description of the excitation energies and transition properties. For the  $E(^2D_{3/2-2}P_{1/2}^{\circ})$  and  $E(^2D_{3/2-2}P_{3/2}^{\circ})$  fine-structure splittings of the three lowest levels of lawrencium, for example, one of the largest MCDF computations (up to the present) have been carried out recently by Zou and Froese Fischer [18], including wave function expansions with more than 330 000 CSF. In these computations, core excitations were treated in a very similar way as the actives space of the valence-shell electrons and were found to be of great significance for the heavy and super-heavy elements.

Although lawrencium has only three valence electrons in the  $7s^27p$  ground state configuration, test calculations reveal quite strong admixtures of those (odd-parity) configurations, for which one of the  $7s$  and  $7p$  electrons are re-placed into the  $6d$ ,  $7d$ ,  $8s$  and  $8p$  subshells. For any reliable prediction of the low-lying level structure of lawrencium as a whole, therefore, these nearly degenerate electron configurations should be appended already to the *list of references*. In the present computations, we incorporated all levels from the  $6d7s^2$ ,  $7s^27p$  and  $6d7s7p$  config-

urations in order to optimize the  $[1s, \dots, 5f, 6s, 6p]$  core electrons as well as the  $\{6d, 7s, 7p\}$  valence electrons. In addition, we also included the spectroscopic configurations  $7s^27d$ ,  $7s^28s$  and  $7s^28p$  into the list of *references*, from which single and double excitations have later been considered [24]. Therefore, to increase the active space for the construction of the CSF, further (correlation) orbitals were optimized as *layers* in a series of steps, where an orbital layer refers to a set of orbitals with the same principal quantum number. This procedure gave rise eventually to a series of approximations with an increasing size,  $n_c$ , of the wave function expansions. In total, two layers of correlation orbitals were taken into account in the present case, including the  $\{9s, \dots, 9h\}$  and  $\{10s, \dots, 10h\}$  orbitals and based on single (S) and double (D) excitations from the reference configurations above. As pointed out by Zou and Froese Fischer [18], especially the  $g$ -orbitals appears to be important for describing the level structure of the (trans-) actinides since these orbitals have a direct dipole interaction with the  $4f$  core orbitals. The  $h$  orbitals, in contrast, already need higher-order interactions in order to contribute to the total energy of the system and are thus less important. For these reasons, however, most of the earlier MCDF computations for the lanthanides and actinides are likely not very reliable because  $g$ -orbitals were often not included *before* the large-scale study in reference [18].

Apart from an estimate on the core-polarization and *core-core* correlations, we usually treated all the odd- and even-parity levels with  $J = 1/2, \dots, 9/2$  together in a single run in order to keep the computations feasible for such a first overview on the level structure of atomic lawrencium. Once having generated all the orbitals, we considered core-polarization and core-core correlation effects by opening the  $\{5f, 6s, 6p\}$  core orbitals for single and the  $\{6s, 6p\}$  orbitals for single and double excitations [25].

Because of the rapid  $(\alpha Z)^4$  increase of the leading QED contributions, a principal source of uncertainty arises also from the scaling of the (one-electron) self-energy (SE) shifts and how they are incorporated into the computations. The vacuum polarization and the next important correction, in contrast, can be taken into account by means of a local Uehling potential [26] and, hence, has been incorporated into relativistic structure calculations for many years by now. In the past, rather different methods have been applied in the literature to scale up the SE data for multi-electron atoms and ion. For predictions on the level structure, fortunately, only the *differences* in the QED shifts are needed with sufficient accuracy and are ‘tested’ eventually by means of optical spectroscopy. Using different model computations for the neutral and weakly ionized ytterbium ( $Z = 70$ ) and nobelium atoms ( $Z = 102$ ), it was shown recently that QED effects alone may lead to an uncertainty of about  $100\text{--}300\text{ cm}^{-1}$  for the excitation energies of all super-heavy elements [13]. But although the theory of QED is now well established as the foundation for all atomic (and molecular) computations, there is — up to the present — no computational procedure in sight which would be feasible to incorporate

**Table 1.** Theoretical excitation energies and absorption rates of the 30 lowest levels of atomic lawrencium with regard to the  $7s^27p\ ^2P_{1/2}^o$  ground levels. All odd- and even-parity levels with total angular momenta  $J = 1/2, \dots, 9/2$  are shown in ascending order of energy. The accuracy of the computations is estimated in column 4 by assigning a group classification to each level;  $\Delta E \lesssim 1200\text{ cm}^{-1}$  (group A);  $\Delta E \lesssim 2400\text{ cm}^{-1}$  (group B);  $\Delta E \gtrsim 2400\text{ cm}^{-1}$  (group C). See text for details. For the absorption rates, only an estimate on the order of magnitude is given and all rates with  $A < 1\text{ s}^{-1}$  with regard to the  $7s^27p\ ^2P_{1/2}^o$  ground level are omitted from the table.

Level designation	$J^P$	Excitation energy ( $\text{cm}^{-1}$ )	Absorption strength (1/s)	Leading configurations in $LSJ$ notation
$7s^27p$	$1/2^-$	0	–	85.8% of $7s^27p\ ^2P_{1/2} + 6.4\%$ of $6d7s(^3D)7p\ ^2P_{1/2}$
$6d7s^2$	$3/2^+$	1331	A	90.0% of $6d7s^2\ ^2D_{3/2} + 2.7\%$ of $6d7p^2\ ^2D_{3/2}$
	$5/2^+$	4187	A	89.6% of $6d7s^2\ ^2D_{5/2} + 2.5\%$ of $6d7p^2\ ^2D_{5/2}$
$7s^27p$	$3/2^-$	8138	B	83.6% of $7s^27p\ ^2P_{3/2} + 5.1\%$ of $6d7s(^3D)7p\ ^2P_{3/2}$
$7s7p^2$	$1/2^+$	20 053	A	59.3% of $7s7p^2\ ^4P_{1/2} + 20.6\%$ of $6d^2(^3P)7s\ ^4P_{1/2}$
$7s^28s$	$1/2^+$	20 405	A	90.1% of $7s^28s\ ^2S_{1/2} + 2.0\%$ of $7p^2(^1S)8s\ ^2S_{1/2}$
$6d7s(^3D)7p$	$3/2^-$	20 886	A	81.5% of $6d7s(^3D)7p\ ^4F_{3/2} + 7.4\%$ of $6d7s(^3D)7p\ ^2D_{3/2}$
	$5/2^-$	23 155	A	74.7% of $6d7s(^3D)7p\ ^4F_{5/2} + 6.9\%$ of $6d7s(^3D)7p\ ^2D_{5/2}$
$7s^28p$	$1/2^-$	25 246	A	48.6% of $7s^28p\ ^2P_{1/2} + 32.1\%$ of $7s^29p\ ^2P_{1/2}$
	$3/2^-$	26 902	A	40.4% of $7s^28p\ ^2P_{3/2} + 24.0\%$ of $7s^29p\ ^2P_{3/2}$
$6d7s(^3D)7p$	$7/2^-$	27 276	B	79.7% of $6d7s(^3D)7p\ ^4F_{7/2} + 10.7\%$ of $6d7s(^3D)7p\ ^4D_{7/2}$
	$5/2^-$	27 794	B	32.7% of $6d7s(^3D)7p\ ^4F_{5/2} + 20.5\%$ of $6d7s(^3D)7p\ ^2D_{5/2}$
	$1/2^-$	27 904	A	76.3% of $6d7s(^3D)7p\ ^4D_{1/2} + 6.4\%$ of $7s^28p\ ^2P_{1/2}$
$7s7p^2$	$3/2^+$	28 312	A	55.0% of $7s7p^2\ ^4P_{3/2} + 33.9\%$ of $6d^2(^3P)7s\ ^4P_{3/2}$
$6d7s(^3F)7p$	$7/2^+$	28 760	C	92.5% of $6d^2(^3F)7s\ ^4F_{7/2} + 4.0\%$ of $6d7s(^3D)7p\ ^4F_{7/2}$
$6d7s(^3D)7p$	$3/2^-$	28 973	B	44.5% of $6d7s(^3D)7p\ ^4D_{3/2} + 16.9\%$ of $7s^28p\ ^2P_{3/2}$
$6d7s(^1D)7p$	$3/2^-$	29 435	A	38.0% of $6d7s(^1D)7p\ ^2D_{3/2} + 22.9\%$ of $6d7s(^3D)7p\ ^2D_{3/2}$
$6d7s(^3F)7p$	$9/2^+$	29 715	C	91.8% of $6d^2(^3F)7s\ ^4F_{9/2} + 4.2\%$ of $6d7s(^3D)7p\ ^4F_{9/2}$
$6d7s(^3D)7p$	$5/2^-$	30 614	A	43.0% of $6d7s(^3D)7p\ ^4D_{5/2} + 16.4\%$ of $6d7s(^1D)7p\ ^2D_{5/2}$
$6d^2(^3F)7s$	$3/2^+$	31 872	C	88.7% of $6d^2(^3F)7s\ ^4F_{3/2} + 3.7\%$ of $6d^2(^1D)7s\ ^2D_{3/2}$
$6d^2(^3F)7s$	$5/2^+$	31 915	C	61.9% of $6d^2(^3F)7s\ ^4F_{5/2} + 13.2\%$ of $6d^2(^3P)7s\ ^4P_{5/2}$
$6d7s(^3D)7p$	$1/2^-$	32 712	B	80.8% of $6d7s(^3D)7p\ ^4P_{1/2} + 7.3\%$ of $6d7s(^3D)8p\ ^4P_{1/2}$
	$9/2^-$	32 775	B	93.1% of $6d7s(^3D)7p\ ^4F_{9/2} + 3.9\%$ of $6d7s(^3D)8p\ ^4F_{9/2}$
	$7/2^-$	33 051	A	73.9% of $6d7s(^3D)7p\ ^4D_{7/2} + 12.1\%$ of $6d7s(^3D)7p\ ^4F_{7/2}$
$6d^2(^3F)7s$	$5/2^+$	33 103	C	29.0% of $6d^2(^3F)7s\ ^4F_{5/2} + 18.8\%$ of $6d^2(^3P)7s\ ^4P_{5/2}$
$6d7s(^3D)7p$	$3/2^-$	33 112	B	63.3% of $6d7s(^3D)7p\ ^4P_{3/2} + 18.3\%$ of $6d7s(^3D)7p\ ^4D_{3/2}$
$6d^2(^3D)7s$	$5/2^+$	33 948	C	66.6% of $6d^2(^3F)7s\ ^2F_{5/2} + 8.8\%$ of $6d^2(^3F)7s\ ^2D_{5/2}$
$6d7s(^3D)7p$	$5/2^-$	33 977	B	40.8% of $6d7s(^3D)7p\ ^4P_{5/2} + 22.4\%$ of $6d7s(^3D)7p\ ^4D_{5/2}$
$6d^2(^1D)7s$	$5/2^+$	34 402	A	37.1% of $6d^2(^1D)7s\ ^2D_{5/2} + 19.4\%$ of $6d^2(^3P)7s\ ^2P_{5/2}$
$6d^2(^1G)7s$	$9/2^+$	34 807	A	83.1% of $6d^2(^1G)7s\ ^2G_{9/2} + 5.9\%$ of $6d7s(^3D)7d\ ^2G_{9/2}$

the self-energy or vacuum polarization into the electronic structure calculations beyond a screened hydrogenic or local-potential model [27]. This is true especially for all (complex) atoms and ions except, perhaps, of those with just a very few electrons such as the helium- or lithium-like ions [20, 28].

### 3 Results and discussions

As mentioned before, nobelium and lawrencium are currently the two most prominent candidates for studying the low-lying level structure of the trans-fermium elements ( $Z > 100$ ). Because of the various difficulties in dealing with SHE, however, the success of all spectroscopic investigations vitally depend on the precision with which the excitation energies of the levels can be predicted in advance theoretically. Beside of the level energies, more-

over, the absorption rates from the corresponding ground state are of immediate relevance in order to ensure a high-enough efficiency in the ion detection scheme. Owing to the available laser systems, the focus of the currently prepared RIS measurements hereby lays on the resonances in the region between 20 000 to 30 000  $\text{cm}^{-1}$  [12].

For a first overview on the low-lying level structure of atomic lawrencium, Table 1 displays the (level) designation, symmetry and excitation energies of the 30 lowest levels with regard to the  $7s^27p\ ^2P_{1/2}^o$  ground level. These energies are based on our ‘best’ wave function expansion from above, including some important core-polarization and core-core correlation contributions. However, no attempt has been made here in order to analyze and display explicitly all individual contributions to the excitation energies. In the last column of Table 1, moreover, we present the leading terms in a  $LSJ$ -coupled CSF basis, having performed a unitary transformation by means

**Table 2.** Comparison of the  $7s^27p\ ^2P_{1/2,3/2}^\circ$  and  $6d7s^2\ ^2D_{3/2,5/2}$  fine structure splitting (in  $\text{cm}^{-1}$ ) with previous computations and experiment.

Method	$^2D_{3/2}-^2P_{1/2}^\circ$	$^2D_{3/2}-^2P_{3/2}^\circ$	$^2D_{3/2}-^2D_{5/2}$	$^2P_{1/2}^\circ-^2P_{3/2}^\circ$
Lutetium				
This work	4417	7593	1643	3176
Vosko and Chevary [16]	3862	–	1580	–
Eliav et al. [17]	3828	7140	1975	3312
Zou and Froese Fischer [18]	4186	7462	–	–
Experiment [32]	4136	7476	1994	3340
Lawrencium				
This work	–1331	6807	2856	8138
Eliav et al. [17]	–1263	7010	3799	8273
Zou and Froese Fischer [18]	–1127	7807	–	–

of the LSJ component [29,30] of the RATIP program [31]. This decomposition of the atomic states shows that the 4 lowest levels are still well classified in a  $LSJ$ -coupled basis but that rather large admixtures may arise for some levels with higher energy.

Even if (almost) nothing is known experimentally so far about the level structure of neutral lawrencium, a critical test is often possible on the quality of the excitation energies by performing analogous computations for the homologous element. The homologous elements usually exhibit a very similar shell structure and, thus, are governed by similar correlation effects. Therefore, in order to explore the theoretical uncertainties of our predictions above, analogue computations have been carried out for atomic lutetium with its low-lying electron configurations  $[4f^{14}5s^25p^6](5d6s^2, 6s^26p, 5d6s6p, 6s^27s, 6s^27p, 6s^26d)$ . Compared with atomic lawrencium, however, lutetium has a  $5d6s^2\ ^2D_{3/2}^\circ$  ground level while, otherwise, we only have to decrease all the principal quantum numbers by one. In this way, lutetium gives rise (exactly) to the same size of the wave function expansions. In practice, of course, further level crossings may occur if the level structure of lutetium and lawrencium is compared in detail, although the number and the extent of these crossings is expected to be moderate. For lutetium, the excitation energies of (most of) the low-lying levels can be compared directly with the experimental (recommended) data as available from the NIST atomic data base [32]. From the analogue computations for lutetium (using again the ‘best’ approximation as described above), three groups of levels can be distinguished, for which the accuracy of the computations,  $\Delta E = |E_{\text{NIST}} - E_{\text{theo}}|$ , is either  $\Delta E < 800\ \text{cm}^{-1}$  (group A) or  $\Delta E < 1600\ \text{cm}^{-1}$  (group B). For a few levels, moreover, either no experimental data are available or the remaining deviations are  $\Delta E \gtrsim 2000\ \text{cm}^{-1}$  (group C). In Table 1, this classification of the levels (owing to the accuracy as achieved for lutetium) is shown in column 4 in order to give an estimate on the expected accuracy of the predicted level energies; for this assignment, of course, the only theoretical justification is that the level structure of homologous elements are typically very similar within the various  $J^P$  symmetry blocks. Because of the strong increase of the relativistic effects, however, the expected ac-

curacy of the various level groups is supposed to be larger by about 50%, i.e. we estimate  $\Delta E < 1200\ \text{cm}^{-1}$  for group A,  $\Delta E < 2400\ \text{cm}^{-1}$  for group B, and even slightly larger uncertainties for the levels of group C.

During recent years, a number of large-scale computations have been carried out for the four lowest levels of atomic lawrencium. Perhaps, the most elaborate one was performed by Zou and Froese Fischer [18] on the  $nd\ ^2D_{3/2} - (n+1)p\ ^2P_{1/2,3/2}^\circ$  fine structure of lutetium ( $n=5$ ) and lawrencium ( $n=6$ ). For lawrencium, in particular, wave function expansions of more than 330 000 CSF were applied and showed that core-core correlations are of great importance for calculating level energies and oscillator strengths. For the four lowest levels of Lu and Lr, therefore, Table 2 compares the level splitting from the present work with experimental data (for lutetium) and with previous computations. Good agreement is found with the computations by Eliav et al. [17] and Zou and Froese Fischer [18], except for the  $E(^2D_{3/2}-^2D_{5/2})$  splitting which, for lutetium, is obtained about 25% lower than NIST recommend value or the work of Eliav et al. [17]. Due to the stability of the ground state configuration, however, all these levels are still expected to fall into the group A also in the case of neutral lawrencium.

Missing correlations are likely the main source of uncertainty in calculating the excitation energies for lutetium and lawrencium. The rather sizeable influence of the core-polarization (and core-core correlations) shows, for instance, that the excitation energies are likely not yet ‘converged’ at the  $\sim 100\ \text{cm}^{-1}$  level of accuracy, but that shifts of a few hundred wave numbers might arise if the size of the wave function expansions could be enlarged further. The same argument applies even more for the absorption rates of the low-lying levels with regard to the  $7s^27p\ ^2P_{1/2}^\circ$  ground level. As discussed especially in reference [18], core-core correlations may influence the oscillator strengths by a factor of 2 and more. In Table 1, therefore, we shall provide only an *estimate* of the absorption rates as obtained in length gauge for the coupling for the radiation field to bound electrons [33]. These rates were calculated by using a restricted wave function expansion in which only the valence-valence correlations were

taken into account. These rates are likely correct with respect to the order of magnitude (as suggested also by the  $\sim 30\%$  agreement of the absorption rates in length and velocity gauge for all dipole-allowed E1 transitions with  $A > 10^7 \text{ s}^{-1}$ ), but should otherwise be used only to guide forthcoming experiments.

Apart from the comparison of the theoretical excitation energies of lutetium with available experimental data, it appears difficult to make any reliable estimate on the *physical* uncertainties of the computations, especially if such a large number of levels is concerned (cf. Tab. 1). Until now, namely, only very little is known about the interplay of the valence-valence, core-polarization and core-core correlation effects for SHE. From the viewpoint of *ab initio* theory, four approximations are prone to introduce uncertainties into the computations. Apart from the (still) rather limited size of the wave function expansions, owing to the restricted active space of spectroscopic and correlation orbitals, the self-consistent optimization on the basis of the Dirac-Coulomb Hamiltonian  $H_{\text{DC}}$ , the truncation of the Dirac-Coulomb-Breit Hamiltonian after the  $\alpha^2$  terms as well as further radiative corrections beyond a screened hydrogenic model might all result in additional uncertainties in the domain of the transeinsteinium elements.

For any accurate prediction of the (optical) excitation energies, of course, the SE shifts of the valence shells must be properly combined with the changes of the effective occupation numbers, including the contributions from the core-valence and core-core correlations. Using the RELCI component [34] of the RATIP code, therefore, we evaluated the SE shifts in a model as suggested originally by Kim [35], using the SE shifts by Mohr [36] and Mohr and Kim [37]. For all other *s*- and *p*-electrons with principal quantum numbers  $n \geq 6$ , a  $n^{-3}$  scaling rule has been applied using the SE shifts from reference [37]. Although the use of a point nucleus (for the calculation of the charge radius) has the advantage that the charge ratio inside of a given sphere of about 40 fm can be computed from analytic formulas, it represents a source of uncertainty and should be replaced with finite-nucleus values in the future. In the model implemented in RELCI, the level energies of lawrencium are affected by up to  $250 \text{ cm}^{-1}$  (and are included in the excitation energies of Tab. 1), while these shifts are still negligible in the case of lutetium. These findings confirm the empirical rule that QED effects are negligible for the valence-shell computations of most stable isotopes. They might become important however for the super-heavy elements with, say,  $Z \geq 100$  and occur — of course — even if the presently available codes do not support very accurate estimates on the self-energy.

In summary, the low-lying level structure of atomic lawrencium has been calculated by using medium- to large-scale MCDF wave functions. Detailed computations have been carried out for the 30 lowest odd- and even-parity levels with total angular momenta  $J = 1/2, \dots, 9/2$ . Table 1 displays the (level) designation, symmetry, excitation energies and absorption rates of these levels with regard to the  $7s^2 7p \ ^2P_{1/2}^\circ$  ground state. As discussed pre-

viously [17,18], there are little doubts today about the  $7s^2 7p \ ^2P_{1/2}^\circ$  ground level of atomic lawrencium (which is in contrast to the  $5d 6s^2 \ ^2D_{3/2}^\circ$  ground state of the homologous lutetium), owing to the relativistic contraction of the *7s* and *7p* orbitals. For most low-lying levels of lawrencium in Table 1, the excitation energies are estimated to be accurate within  $1200 \text{ cm}^{-1}$  (group A) or  $2400 \text{ cm}^{-1}$  (group B). For a few other levels from group C, moreover, the level energies appear rather sensitive to the size of the wave expansion or they are simply unknown for lutetium; in both of these cases, we estimate the uncertainties of these energies to about  $\Delta E \gtrsim 2000 \text{ cm}^{-1}$  to give a conservative boundary. Providing a quite large number of energies, however, a critical test on the ‘quality’ of the present-day predictions might become possible soon already — if they will be confirmed or discarded by experiment [12].

Apart from the excitation energies and absorption rates of the low-lying levels with respect to the ground state, ion radii measurements have attracted recent interest [10]. From the drift time of the ions in the electric field of a buffer gas cell, for example, the ratios of the ionic radii of  $r_{\text{Fm}^+}/r_{\text{Cf}^+}$  and  $r_{\text{Pu}^{2+}}/r_{\text{Cf}^+}$  were deduced [38]. In fact, the relativistic shrinking of the valence orbits has been studied for atoms already earlier [39] and should be reflected directly by means of the ion mobility. Caused by the change of the electron configuration in going from No to the  $[\text{Rn}] 5f^{14} 7s^2 7p$  ground configuration of Lr, a decrease in the atomic radii  $r_{\text{Lr}^+}/r_{\text{No}^+} = -8\%$  has been predicted [39], from which about 20% can be attributed to relativistic effects. To investigate this shrinkage of the charge density also experimentally, a dedicated buffer gas cell has been proposed for the SHIPTRAP facility and will provide a unique possibility to test the predictions up to heaviest actinides elements which, otherwise, are accessible only by chemical methods. In addition, once the excited levels are known for some elements, they can be utilized in addition in order to determine the hyperfine structure. In this way, nuclear ground-state properties, such a *g*-factors, quadrupole moments or changes in the charge radii can be derived.

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