Resonance Transition Energies and Oscillator Strengths in Lutetium and Lawrencium

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The transition energies and oscillator strengths for $nd\ ^2D_{3/2} - (n + 1)p\ ^2P^o_{1/2,3/2}$ transitions in Lu ($n = 5$, $Z = 71$) and Lr ($n = 6$, $Z = 103$) were calculated with the multiconfiguration Dirac-Hartree-Fock method. The present study confirmed that the ground state of atomic Lr is $[\text{Rn}]5f^{14}7s^27p\ ^2P^o_{1/2}$. The calculation for Lr required wave function expansions of more than 330 000 configuration states. In Lu, the transition energies, with Breit and QED corrections included, agree with experiment to within 126 cm^{-1}. In lighter elements, core correlation is usually neglected but was found to be of extreme importance for these heavy elements, affecting the oscillator strengths by a factor of 3 and 2 in Lu and Lr, respectively.

The calculation of heavy atoms requires a proper treatment of both relativistic effects and electron correlation, resulting in large configuration state function (CSF) expansions in the multiconfiguration Dirac-Hartree-Fock (MCDHF) approach [1]. The large expansions challenge the computational method as well as modern computers. It is highly desirable to develop and cross check the theoretical methods for calculating energies and oscillator strengths of heavy elements with nuclear charge greater than 100 since direct measurements are very difficult at the moment. The transition energy $E(^2D_{3/2} - ^2P^o_{1/2})$ of lawrencium ($Z = 103$) between the $[\text{Rn}]5f^{14}7s^26d\ ^2D_{3/2}$ and $[\text{Rn}]5f^{14}7s^27p\ ^2P^o_{1/2}$ levels has been investigated using semiempirical [2–4] and multiconfiguration Dirac-Hartree-Fock [5,6] methods, and the relativistic coupled cluster theory [7]. The reported values range from 0.0 to -8.0×10^3 cm^{-1} and no experimental data have been published. Lutetium ($Z = 71$) is the heaviest element with an analogous shell structure, $[\text{Xe}]4f^{14}6s^25d\ ^2D_{3/2}$ and $[\text{Xe}]4f^{14}6s^26p\ ^2P^o_{1/2}$, and may provide a benchmark for the study of Lr as well as a calibration for the energy accuracy.

In the present work, the transition energies and the oscillator strengths of $nd_{3/2} - (n + 1)p_{1/2,3/2}$ transitions for the atoms Lu ($n = 5$, $Z = 71$) and Lr ($n = 6$, $Z = 103$) were calculated.

The multiconfiguration Dirac-Hartree-Fock (MCDHF) approach [1] is adopted in these calculations. The wave function of an atomic system can be expanded as a linear combination of CSF's,

$$\Psi(\alpha J\pi) = \sum_j C_j \Phi(\alpha_j J\pi), \qquad (1)$$

where J and π are the total angular momentum and parity of the system, respectively, α_j is a set of quantum numbers to specify a CSF additional to $J\pi$, and C_j is the mixing coefficient. A CSF, $\Phi(\alpha_j J\pi)$, is constructed from a product of single electron wave functions through a proper angular momentum coupling and anti-symmetrization. The MCDHF self-consistent iteration method is used to obtain

simultaneously the mixing coefficients and the radial orbitals. The Dirac-Coulomb Hamiltonian of a many electron atomic system is assumed in the variational process. The finite-nucleus effect is taken into account by assuming an extended Fermi distribution for the nucleus. Based on these orbitals, a configuration interaction calculation may be performed to include the Breit interaction and QED effects. Here the orbitals are fixed but the mixing coefficients are recalculated by diagonalizing the modified Hamiltonian.

Once the initial and final state wave functions have been calculated, the radiative transition matrix element can be obtained from

$$M_{if} = \langle \Psi(i)||O^{(1)}||\Psi(f)\rangle, \qquad (2)$$

where $O^{(1)}$ is the electric dipole interaction. For the large expansion including core correlation, Ψ was approximated by discarding the CSF's with mixing coefficient smaller than 10^{-6}. This approximation was tested for a smaller expansion with only core-valence correlation.

The graspVU code, a modified and parallel version of GRASP92 [1], is used to calculate the wave functions of the atomic system and the transition matrix elements. The occupied orbitals were obtained from the Dirac-Hartree-Fock (DHF) calculation in even and odd parities separately to take into account the effect of orbital relaxation. The correlation orbitals were optimized layer by layer in four different expansions. Orbital sets with the same principal quantum number are referred to as a layer. Since the orbitals for the upper and lower states of a transition are obtained from separate optimizations, the biorthonormal technique [8,9] is applied to make the orbitals biorthonormal and then the standard Racah algebra can be used in the calculations of transition matrix elements.

First of all, the calculations for Lu were performed to investigate the optimizing schemes for the orbitals and the various correlations that are described by including corresponding CSF's. By increasing the maximum orbital angular momentum from f to h, it was found that g orbitals were very important for the transition energy

$E(^2D_{3/2} - {}^2P^o_{1/2})$ but h orbitals were relatively unimportant. This can be understood from the fact that g orbitals have a direct dipole interaction with $4f$ core orbitals whereas h orbitals have higher order interactions. Therefore, the earlier calculations [6] with MCDHF for Lu and Lr are not reliable since g orbitals were not included in the expansion.

With a set of fixed orbitals, the effects of triple excitation from the valence, triple and quadruple excitation from the core of the single reference configuration, and the single and double excitations of multireference configurations were examined. The transition energies did not change significantly by including the CFS's from such excitations.

The transition energies of $nd\ ^2D_{3/2} - (n + 1)p$ $^2P^o_{1/2,3/2}$ as well as the correction of the Breit interaction with the low frequency approximation and the QED effects including the vacuum polarization, mass polarization [1], and self-energy correction [11–14] are listed in Table I. The Breit and QED corrections were estimated in the DHF approximation. It appeared that neither had a large effect. In comparing results given in Table I, it is important to remember that the present transition energies do not include the Breit or QED corrections. The relativistic coupled cluster calculation by Eliav *et al.* [7] gave both with and without the low frequency Breit correction for Lr. The differences of $125/50$ cm^{-1} for $E(D_{3/2} - P_{1/2})/E(D_{3/2} - P_{3/2})$ are in a fair agreement with the present DHF estimation of $97/4$ cm^{-1}. It also can be noticed that the QED effects tend to cancel the Breit correction.

In the first calculation for Lu, the CSF's from single and double excitation of the valence $6s^25d/6s^26p$ orbitals were included to take into account the valence (VV) correlation. The core-valence (CV) correlation was approximated by the additional CSF's with one electron excited from the $4f$ core and another from a valence orbital. It was noticed from a separate calculation that the $6s$ valence-core interaction has very little effect on the transition energies. Those CSF's were not included in the expansion. The calculated $5d_{3/2} - 6p_{1/2}$ transition energy of 3989 cm^{-1} is in a good agreement with that of observation, 4136 cm^{-1} and other calculations from relativistic coupled cluster (RCC). Oddly enough, the density functional theory (DFT) results are reasonably close to the present value. However, when $5p$ core-valence correlation was included in a second calculation, the transition energy was overestimated by about a factor of 2. This result was not changed by the further inclusion of $5s, 4d$ core-valence correlation. The situation was similar for the $5d_{3/2} - 6p_{3/2}$ transition.

To investigate the effect of core correlation (CC), a preliminary large scale configuration interaction (CI) calculation was carried out with the additional CSF's generated from single and double excitations from the $5p$ and $4f$ core, using radial orbitals from the smaller scale valence correlation study. Following this calculation, the CSF's with the mixing coefficient greater than 10^{-4} were retained in a self-consistent field calculation to optimize the correlation orbitals. With this set of orbitals, a CI calculation with all the CSF's was performed to include $5p$ and $4f$ core correlation as well as core-valence and valence correlation. This third calculation brought the transition energy back to

TABLE I. The transition energies in cm^{-1} of $nd\ ^2D_{3/2} - (n + 1)p\ ^2P^o_{1/2,3/2}$ and the size of CSF expansions for Lu ($n = 5$) and Lr ($n = 6$).

Expansion	$^2D_{3/2} - {}^2P^o_{1/2}$	$^2D_{3/2} - {}^2P^o_{3/2}$	CSF ($^2D_{3/2}/^2P^o_{1/2}/^2P^o_{3/2}$)
Lu			
VV + CV($4f^{14}$)	3989	7276	4354/2071/3813
VV + CV($5p^64f^{14}$)	8004	11 483	5600/2764/5073
VV + [(CV + CC)($5p^64f^{14}$)]	3857	7130	128 763/36 974/100 277
VV + [(CV + CC)($4d^{10}5s^25p^64f^{14}$)]	4186	7462	305 717/87 241/236 554
RCC [7]	3828	7140	
DFT [10]	3862		
Exp.	4136	7476	
DHF Breit Correction	87	53	
DHF Breit & QED Correction	76	43	
Lr			
VV + CV($5f^{14}$)	−1298	9137	3659/1842/3338
VV + CV($6p^65f^{14}$)	1339	12 761	4708/2495/4495
VV + [(CV + CC)($6p^65f^{14}$)]	−1953	6469	125 325/37 333/97 500
VV + [(CV + CC)($5d^{10}6s^26p^65f^{14}$)]	−1127	7807	330 252/95 969/246 376
RCC	−1388	6960	
RCC with Breit	−1263	7010	
DHF Breit Correction	97	4	
DHF Breit & QED Correction	59	−26	

3857 cm^{-1}. In the fourth calculation, the $4d$ and $5s$ core in addition to the $5p$ and $4f$ core were opened for single and double excitations. The orbitals with the principal quantum number $n = 8-9$ were reoptimized with the same approach as in the third calculation. The transition energy of $5d_{3/2} - 6p_{1/2}$ was improved to 4186 cm^{-1}. Similarly, the $5d_{3/2} - 6p_{3/2}$ transition energy became 7462 cm^{-1}.

By comparing the oscillator strength results with and without the core correlation in Table II, one can find that core correlation affects the scaled oscillator strength by about a factor of 3. The scaled oscillator strength was defined as $gf_{\text{scale}} = gf_L E_{\exp}/E_{\text{th}}$. It also can be noticed that the gauge difference is large for both cases with and without core correlation. However, as the cores of $4d$ and $5s$ were opened in the fourth calculation, the agreement was improved. This result indicates that the gauge difference may be caused by the incomplete treatment of correlation.

With the same strategy as used in Lu, we calculated the transition energies and oscillator strengths for Lr with a similar shell structure as in Lu except for a larger core. The results are shown in the second half of Tables I and II, respectively. When only $5f$ core-valence and valence correlation were included, the transition energy of $E(^2D_{3/2} - {}^2P^o_{1/2})$ was -1298 cm^{-1}. When additional $6p$ core-valence correlation was taken into account, $E(^2D_{3/2} - {}^2P^o_{1/2})$ changed sign to become $+1399 \text{ cm}^{-1}$. By including $5f$, $6p$ core correlation, $E(^2D_{3/2} - {}^2P^o_{1/2})$ was inverted back to -1953 cm^{-1}. When we also included $5d$, $6s$ core correlation, $E(^2D_{3/2} - {}^2P^o_{1/2})$ was improved to -1127 cm^{-1}, in reasonable agreement with the RCC value of -1388 cm^{-1}. The result for $6d_{3/2} - 7p_{3/2}$ transition was similar to that of $6d_{3/2} - 7p_{1/2}$ but the present transition energy was about 900 cm^{-1} higher than that of RCC. The latter used a finite analytic basis, the number of basis orbitals being the same for Lu and Lr. At first sight, this seems suspect in that Lr has more occupied orbitals. In the present work, orbitals are represented numerically, optimized, and an

extra layer of orbitals used for Lr. Although the RCC calculation included some triple and quadruple excitations effectively through linked expansion, those excitations are not important in the present case according to our separate test calculations. It was also verified in Lu.

The oscillator strengths for Lr are shown in the second half part of Table II. The gauge dependence increased for the $^2D_{3/2} - {}^2P^o_{1/2}$ transition when compared with Lu, but decreased for the $^2D_{3/2} - {}^2P^o_{3/2}$ transition.

The sizes of the expansions are also shown in Table I. In the VV + CV calculations, the active orbitals were up to $8h$ for Lu and $9g$ for Lr. In the VV + CV + CC calculations, the active orbitals were up to $9g$ for Lu and $10g$ for Lr. The largest calculation of 330,252 CSF (as well as others) was performed on the IBM SP2 parallel computer at NERSC, using 120 processors.

In summary, we have calculated the transition energies and oscillator strengths of $nd \; {}^2D_{3/2} - (n + 1)p \; {}^2P^o_{1/2,3/2}$ for Lu ($n = 5$, $Z = 71$) and Lr ($n = 6$, $Z = 103$). It was found that core correlation is significant for the transition energies and oscillator strengths. Without core correlation, the transition energy $E(^2D_{3/2} - {}^2P^o_{1/2})$ was over estimated by a factor of 2 for Lu. The final energies, including $4d$, $5s$, $5p$, $4f$ core correlation agree to well with those of experiment and other theory. For Lr, experimental energies are not available, but without core correlation, the transition energy $E(^2D_{3/2} - {}^2P^o_{1/2})$ was inverted. The results including $5d$, $6s$, $6p$, $5f$ core correlation are in a good agreement with those of the RCC calculation, considering the sensitivity of the transition energy to correlation, but the agreement is not nearly as good as for Lu. The present calculation confirmed that the ground state of atomic Lr is $[\text{Rn}]5f^{14}7s^27p \; {}^2P^o_{1/2}$. For the oscillator strengths, the core correlation that is usually neglected in lighter elements, affect the values by a factor of 3 and 2 in Lu and Lr, respectively. Also, the gauge dependence is significant. It may be improved by including additional inner core correlations.

TABLE II. The oscillator strengths of $nd \; {}^2D_{3/2} - (n + 1)p \; {}^2P^o_{1/2,3/2}$ for Lu ($n = 5$) and Lr ($n = 6$).

Expansion	$^2D_{3/2} - {}^2P^o_{1/2}$			$^2D_{3/2} - {}^2P^o_{3/2}$		
	gf_L	gf_V	Scaled gf_L	gf_L	gf_V	Scaled gf_L
Lu						
VV + CV($4f^{14}$)	0.0304	0.0582	0.0315	0.0111	0.0219	0.0114
VV + CV($5p^64f^{14}$)	0.0511	0.1552	0.0264	0.0144	0.0467	0.0094
VV + [(CV + CC)($5p^64f^{14}$)]	0.0908	0.3835	0.0974	0.0322	0.0856	0.0337
VV + [(CV + CC)($4d^{10}5s^25p^64f^{14}$)]	0.1043	0.3345	0.1031	0.0354	0.0742	0.0355
Lr						
VV + CV($5f^{14}$)	−0.0162	−0.0076		0.0210	0.0313	
VV + CV($6p^65f^{14}$)	0.0144	0.2359		0.0227	0.0839	
VV + [(CV + CC)($6p^65f^{14}$)]	−0.0624	−0.0002		0.0414	0.0867	
VV + [(CV + CC)($5d^{10}6s^26p^65f^{14}$)]	−0.0378	−0.0024		0.0519	0.0685	

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