atoms

Article

Configuration–Interaction Perturbation Theory Calculations of Pu II

Igor Savukov

Los Alamos National Laboratory, Los Alamos, NM 87545, USA; isavukov@lanl.gov

Received: 18 June 2020; Accepted: 28 July 2020; Published: 30 July 2020

Abstract: Configuration–interaction perturbation theory (CI–PT) is applied to calculations of low-energy states of Pu II. This ion is quite challenging due to a large number of possible determinants arising from seven valence electrons and strong relativistic effects. The CI–PT calculations agree with experiments for the energies and g-factors for many low-energy states that allowed positive identification of the theoretical levels. Isotope shifts were also used to aid in identification, and, in case of the odd states, fitting with three independent parameters was used to match theoretical isotope shifts to the experimental values with good accuracy. The CI–PT approach tested here on the Pu II ion can be generally used to calculate properties of many complex atoms, including U I that can find application in fundamental and applied science.

Keywords: CI-PT; configuration-interaction perturbation theory; g-factors; isotope shifts; Pu II

---

1. Introduction

Plutonium is an important actinide element, used in many applications such as nuclear weapons and nuclear energy. The detection of Pu in various materials and characterization of its isotopic content are needed in nuclear forensics, analysis of nuclear fuels, diagnosis of nuclear reactors, and many other applications [1–5]. Specifically, Pu isotopes can be accurately characterized with laser absorption techniques in combination with laser ablation for which knowledge of atomic properties such as hyperfine structure and isotope shift is needed [6]. Frequently used in Pu characterization applications, laser-induced breakdown spectroscopy (LIBS) also needs theoretical input, especially transition probabilities, lifetimes, and state population distributions, since the excitations of many levels in this method lead to complex spectra with a large number of lines merged.

Many theories, such as relativistic many-body perturbation theory (MBPT), or a combination of configuration interaction with MBPT (CI-MBPT) were not applied to Pu and many similar atoms and ions, while such theories are quite promising. In the case of CI-MBPT, while this theory includes most important relativistic effects [the Dirac Hartree–Fock (DHF) basis set] and valence–core interactions (in the second-order of MBPT), it has an additional problem in atoms with more than two valence electrons that it is difficult to saturate valence–valence interactions. Some solution to this problem was the introduction of scaling parameters, so that agreement with experiments for energies was substantially improved, for example in case of U III and Th I, allowing matching theoretical and experimental levels [7,8]. Another approach was to replace in CI-MBPT the second-order MBPT with all-order MBPT corrections, in the so-called CI-all-order method. It was found that this *ab initio* method can reproduce well energies and g-factors, but the method is computationally challenging [7] and had limited success in neutral uranium, as we found in our preliminary calculations.

While Cowan's code [9] based parametric calculations are able to reproduce energies quite well, they do not give accurate wavefunctions, and, to improve the wavefunctions and transition data accuracy, polarization potentials were introduced to achieve reasonable agreement with experiment: in La II [10] and U II [11] for strong lines. In case of La II, it can be seen that better accuracy is achieved using the CI-MBPT approach with a relatively small number of adjustable parameters to scale the second-order MBPT to improve the accuracy of valence–core interactions [12]. Another problematic issue with Cowan's code is that relativistic effects are not consistently included, but only through scaling of the spin–orbit term. Most consistent treatment of relativistic effects has been done in total energy calculations for a large number of atoms, including Pu II [13].

In addition to methods based on atomic structure codes, approaches based on molecular structure codes are also possible and have been applied to calculations of some properties of actinides [14–18]. In particular, correlating basis sets for actinide atoms have been used to predict transitions energies, such as the 6d-5f energy [14], and the basis of atomic natural orbitals was developed for actinides and applied for calculations of ionization potentials (not applied to the analysis of excited states) [15]. The chemical structure calculations are needed for the analysis of chemical properties of Pu and other actinides.

Motivated by needs of weapons research and characterization, Pu I and Pu II spectroscopic information had been acquired over many years [19–25] and currently a large number of lines as well as energy levels have been identified. In addition to wavelength measurements and intensities, g-factors and isotope shifts (IS) played an important role in the identification of levels. A large collection of data are reported in [26], with which we will compare our calculations. (Note that throughout the paper we adopt IS units of 10^{-3} cm^{-1} or mK, and IS between ^{239}Pu and ^{240}Pu.) The constant ratios can be used to obtain IS for other isotopes.

Because IS of Pu are strongly dependent on the configurations but only weakly on fine structure components, J and coupling schemes, they can be used to determine the principle configurations and the next leading configurations purely from the experiment rather than from theoretical interpretation based on parametric fitting. It has been shown that a linear correlation [27] exists between the IS and the total density of s electrons near the nucleus $4\pi\psi_s^2(0)$ obtained by summing the contributions from all of the s orbitals each being weighted by its occupation number (non-relativistic calculations [28] and relativistic calculations [27]) for different configurations, which can be explained by the screening of s electrons by the other electrons. The IS consists of the normal mass shift $-m/(m+M_A)$, which depends on the mass of the isotope M_A only, where m is the mass of the electron, the specific mass shift $M_A/(2(M_A+m)^2) < \sum_{i\neq j} p_i p_j >$, where p_i is the electron momentum in the infinite nuclear mass system, and the field shift. In the Pu atom, the field shift $\delta E = -F\delta < r^2 >$, where $\delta < r^2 >$ is the change in the root-mean-square radius of the nucleus, is larger than the specific mass shift, and will approximately determine the dependence of IS on particular configurations and states. This might be a general rule for heavy atoms, since their nuclear sizes as well as the density of electrons at the nucleus, especially of s electrons, increases. A detailed calculation of mass and field shifts in [29] for Cs and Fr provides some estimate for Pu II. Fr 7s electron is analogous to the Pu II 7s electron, and the field shift of the Fr 7s electron is much larger than that of Cs 6s electron, where the mass shift is still important.

Preliminary classification of levels was done using the IS method [30], where theoretical studies of Pu II were conducted [30]. There are also calculations of the ionization potential of the 7s state [16,17,31].

It is interesting that there are regularities and similarities in the energies of lowest configurations of lanthanidies and acinides. For example, the energy required to promote an electron from a 4f to 5d or from a 5f to 6d orbitals varies rapidly in irregular manner as nuclear charge increases, but a large portion of the variation and most of the irregularity can be attributed to the pairing energy within the f core. Nugent and Vander Sluis [32] were even able to assume that the energy of a given f^q core as obtained from the data for the trivalent ions could be used unchanged in calculating energies of the neutral atoms. Brewer [33] tabulated lowest energies of various configurations using this method and experimental measurements for low-charge ions of actinides. These configuration energies were used in our calculations to adjust configuration expansions to achieve correct results in the first approximation.

2. Theory

Pu II ion with seven valence electrons is quite challenging for *ab initio* theory. Because the number of determinants (possible states) grows very fast with the number of included orbitals, it is almost impossible to saturate the basis in valence–valence configuration–interaction (CI) space. However, a method of configuration–interaction perturbation theory (CI–PT) is well suited for cases of many valence electrons [34] and can be applied. The main idea is to split large valence–valence CI space into a small strongly interacting manifold, which can consist of a few principal configurations, and the complementary space, with its contributions included via second-order perturbation theory. This is quite similar to CI-MBPT, where the complementary space includes core excitations. Unlike CI-MBPT, the CI–PT approach is not limited to the case where valence and core states are clearly separated. In order for the CI–PT approach to be efficient, it is necessary to use a starting valence-electron potential that takes into account a significant portion of interaction between valence electrons in zero order. In case of Pu II, we chose to include the $5f^6$ electrons into the starting potential, resulting in the dominance of the principal configurations, with relatively small perturbation corrections in the CI–PT method, leading to proper convergence of the perturbation corrections. Such an initial potential is almost ideal for even states of type $5f^6nl$, but somewhat less optimal for odd states that have $5f^5n_1l_1n_2l_2$ configurations. Still, the CI–PT method can improve the accuracy by including excited states that correct orbitals to make them approach the physical orbitals. While it is possible to use multiple starting potentials, optimized for each specific configuration, it would be a cumbersome procedure for calculations and, in some cases, when transition amplitudes are needed, the same potential has to be used, at least within the available CI–PT code. One motivation of the current calculations is the test of the CI–PT method on the atomic system that has limited options for *ab initio* calculations. Since the code is also relativistic, based on DHF starting potential and basis sets, it can be applied to various problems that are of great interest to fundamental and applied physics.

The CI–PT theory is described in [34]. In the valence CI approach, the valence electrons, which are above the core electrons in energy, are treated using the CI method. The wave function for a state number m for valence electrons has the form of expansion over single-determinant basis states,

$$\Psi(r_1,...,r_{N_e}) = \sum_i c_{im}\Phi_i(r_1,...,r_{N_e}) \tag{1}$$

The coefficients of expansion c_{im} and corresponding energies E_m are found by solving the CI matrix eigenstate problem,

$$(H^{CI} - EI)X = 0, \tag{2}$$

where I is the unit matrix, the vector $X = \{c_1,...,c_{N_s}\}$, and N_s is the number of many-electron basis states. The basis states $\Phi_i(r_1,...,r_{N_e})$ are obtained by distributing N_e valence electrons over a fixed set of single-electron orbitals. The number of basis states N_s grows exponentially with the number of electrons N_e (see, e.g., [35]), and the CI matrix quickly becomes too large if the number of electrons exceeds four. Thus, in case of Pu II, the CI method will be technically difficult to implement. All many-electron basis states can be divided into two groups, the first P that contains the N_{eff} low-energy states which dominate in the expansion (1) and the second that contains the high-energy states Q. The effective Hamiltonian $\langle i|H^{CI}_{eff}|j\rangle$ for P space can be written as:

$$\langle i|H^{CI}_{eff}|j\rangle = \langle i|H^{CI}|j\rangle + \sum_k \frac{\langle i|H^{CI}|k\rangle\langle k|H^{CI}|j\rangle}{E^{(0)} - E_k} \tag{3}$$

Here, i, j states are in P, while k states are in Q. Thus, the number of calculations for the full CI Hamiltonian matrix $N_s \times N_s$ is reduced to $N_{eff} \times N_s$ that is by N_s/N_{eff} times and the eigenvalue solution is needed only for a much smaller matrix $N_{eff} \times N_{eff}$. The energy $E^{(0)}$ is chosen initially as the solution of the CI equation without the PT part (the second term in Equation (3)). Then, the PT part is added and the new set of energies is obtained. This procedure is iterated until convergence at the level of a few inverse cm is achieved. In our calculations, we set 10 as the maximum number of iterations, and, in most cases, three iterations were sufficient. For CI–PT theory to work well, it is important to find a starting potential that would minimize the perturbation contributions and assure the perturbation convergence. In case of Pu II, we found that $5f^6$ valence electrons can be included into the initial approximation to reduce the PT part. This starting potential is most proper for states of even parity, for example $5f^67s$, while odd parity states of type $5f^5n_1l_1n_2l_2$, where n_1,n_2,l_1, and l_2 are the principal numbers and orbital moments of two valence states, e.g., $6d7s$, are less accurately approximated, but still it is possible to improve accuracy by using expansion over f states in the CI–PT method.

The configurations included into the CI–PT calculations will be described for each parity separately.

In terms of specific numerical steps, first, the DHF V^{N-1} potential containing $5f^6$ valence electrons is calculated. Second, the basis in the frozen V^{N-1} potential is calculated with the help of a B-spline subroutine for the ion in a cavity of radius $R = 20$ a.u. The basis is then used to evaluate the CI–PT terms in Equations (1)–(3), with the PT part being the second term in Equation (3). The eigenvalue problem (Equation (2)) is solved for the effective Hamiltonian (Equation (3)).

3. Calculations

3.1. Lowest-Energy Even State Calculations

It is difficult to saturate contributions from possible excited states when there are seven valence electrons even using B-spline basis sets for an ion in a cavity which requires the maximum principal number of 17 for each angular momentum, so preliminary calculations were performed to find sets of configurations that can approximately give energies of the lowest states. For example, when the $5f^67s$ state with J = 0.5 is calculated, single excitations from $5f$ to nf are included with n up to 17 and from $7s$ to ns with n up to 14. Similarly, for the $5f^66d$ J = 1.5 state, single excitations described in Table 1 are included. With such high n, the single excitations of this type were saturated, and such excitations preserving symmetry are of monopole type (L = 0) and are important even if excitation energy is not very small. The symmetry preserving excitations essentially correct the starting potential. On the other hand, when many excitations are possible and it is known that with proper physical wavefunctions a single configuration approximation should work, the excitations of this type are most proper. The other states considered in Table 1 do not need extensive expansion because they already have significant energy and would have only weak mixing with the most basic configurations, $5f^67s$ and $5f^66d$, which can be assigned to low-energy even states of Pu II. The most important consideration was to have the energies of these configurations approximately correct, so in some cases more excitations were included. Because some mixing of states of different symmetry is possible, in the preliminary calculations that are presented in Table 1, only approximate energy agreement was sought. For example, even though the energy of the current theoretical lowest J = 2.5 $5f^57s7p$ state deviates from energies in Ref. [30,33], if it is mixed with low f^67s or f^66d states, the effect of the mixing on the energy of $5f^67s$ or $5f^66d$ states will be quite small. Once the configurations listed in the table were separately tested, they were combined into a large set, which led to inclusion of configuration mixing of different symmetry: e.g., $5f^67s$ with $5f^57s7p$, etc.

Table 1. CI–PT energies and g-factors of lowest even single-configuration states: [a] the experimental energies, g-factors, and IS taken from [30,33], where proper configuration assignment was made. Single excitations "SE" from the basic CI–PT configurations in "Conf." are restricted by specifications in "Exc. Conf." column. The reference state, that is the state in which energy is set to zero, is $5f^67s$.

J	Conf.	Exc. Conf.	E_{CI-PT}	E [a]	g_{CI-PT}	g [a]	IS [a]
0.5	$5f^67s$	SE 17f, 14s	0	0	3.7192	3.15	381
1.5	$5f^66d$	SE 17f, 13d	9718	12,008	−0.2749	−0.019	77
2.5	$5f^57s7p$	No exct.	34,285	30,956			
2.5	$5f^57s7p$	SE 9f, 11s, 11p	28,366	30,956	0.1781	0.646	424
4.5	$5f^56d7p$	SE 6f, 7d, 8p	33,003	33,793	0.4624	0.8	208
5.5	$5f^46d^27s$	$5f^46dnd7s$, n = 7–14	43,465	37,641	0.5219	0.7	813

3.2. Energy Levels, g-Factors, IS, and Dominant Configurations of the Pu II Even States

Using the set of non-relativistic configurations specified in Table 2, which was derived from Table 1, we calculated energy levels of some low even J = 1/2–11/2 states (Tables 3–8). The experimental and theoretical energies were rounded to the nearest whole number of cm^{-1}. The order of theoretical energies was changed in some cases to match the configuration labels derived from experimental IS values. For example, in Table 3, the fourth and fifth theoretical levels that have quite close energies and are strongly mixed were exchanged to match leading configurations derived from IS: the $5f^6 6d$ from IS = 79, and $5f^6 7s$ from IS = 357. The incorrect theoretical mixing of these states, which is due to limited theoretical precision, lead to disagreement between theoretical and experimental g-factors, although since only these two levels strongly interact, the sum of theoretical g-factors 0.674 is close to the sum of experimental values 0.718. The other theoretical levels do not exhibit such a strong mixing and their g-factors are in good agreement with the experiment. A similar situation is in the case of J = 1.5, where it is also necessary to swap the fourth and fifth levels to match dominant experimental and theoretical configurations and g-factors. However, the mixing between these levels is weaker and, after swapping, theoretical and experimental g-factors for all six levels agree relatively well. Still, it appears that some mixing exists between the third and the fifth levels, and their sum agrees well between theory and experiment: 2.099 vs. 1.906. Seven energies and six g-factors of J = 2.5 states are all consistently in good agreement with experiment; however, the seventh level should be $5f^6 6d$ rather than $5f^6 7s$ according to its IS value, although a somewhat large value 153 of the fifth level with the dominant configuration $5f^6 6d$ indicates an admixture of $5f^6 7s$ configuration which has an IS of about 391. In the case of J = 3.5, the theory agrees with experiments quite well, but, for higher states to align well, it is necessary to assume that one experimental level is missing. Similarly, for a close agreement between theory and experiment, it is necessary to assume that one J = 5.5 state is missing too. In the case of J = 6.5, too few states are available for comparison.

In general, the agreement between theory and experiment for lowest even states is reasonable, considering that the theory did not have adjustable parameters. Further work is needed to see if some levels are indeed missing, or the presence of unaccounted level is a theoretical artifact.

Table 2. Set of 70 non-relativistic configurations chosen for even states.

$5f^6 ns$, $n = 7..14$	$5f^6 nd$, $n = 6..13$	
$5f^4 6dnd7s$, $n = 6..14$	$5f^4 6d^2 nd$, $n = 6..14$	$5f^4 nd7s^2$, $n = 6..14$
$5f^5 7p6d$	$5f^5 7p7s$	
$5f^5 nf6d$, $n = 6..17$	$5f^5 nf7s$, $n = 6..17$	
$5f^4 7p^2 7s$	$5f^4 7p^2 6d$	

Table 3. Energy levels and g-factors of J = 0.5 even states. The experimental configurations "Conf[expt]" are derived from IS, since $5f^6 7s$ corresponds to 381, while $5f^6 6d$ to 77. The order of the 4th and 5th CI–PT energies was changed to match the configuration labels derived from experimental IS values. g_{obs2} are from [36].

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	g_{obs2}	IS	Conf[expt]
0	0	0	$5f^6 7s$	3.583	3.15	3.139	381	$5f^6 7s$
3236	3118	−117	$5f^6 7s$	−0.194	0.299	0.304	365	$5f^6 7s$
10,188	11,966	1777	$5f^6 7s$	2.550	2.402		385	$5f^6 7s$
14,693	16,683	1990	$5f^6 7s$	0.331	0.84		357	$5f^6 7s$
16,287	16,253	−33	$5f^6 6d$	0.343	−0.122		79	$5f^6 6d$
18,518	18,111	−407	$5f^6 6d$	2.716	2.755		77	$5f^6 6d$

Table 4. Energy levels and g-factors of J = 1.5 even states. The experimental configurations "Conf[expt]" are derived from IS, since $5f^67s$ corresponds to 384, while $5f^66d$ to 77. The order of the 4th and 5th CI–PT energies was changed to match the configuration labels derived from experimental IS values.

E_{exp}	E_{CI-PT}	dE	Conf[CI–PT]	g_{CI-PT}	g_{obs}	g_{obs2}	IS	Conf[expt]
2015	2015	0	$5f^67s$	1.927	1.881	1.883	384	$5f^67s$
5502	5656	154	$5f^67s$	1.134	1.169	1.168	364	$5f^67s$
12,008	12,136	128	$5f^66d$	−0.249	−0.019		77	$5f^66d$
13,991	16,320	2329	$5f^67s$	1.756	1.728		382	$5f^67s$
14,433	14,747	313	$5f^66d$	2.348	1.925		81	$5f^66d$
17,040	17,639	600	$5f^66d$	1.305	1.354		81	$5f^66d$

Table 5. Energy levels and g-factors of J = 2.5 even states.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	g_{obs2}	IS	Conf[expt]
3970	3970	0	$5f^67s$	1.6865	1.67	1.67	391	$5f^67s$
7498	7848	350	$5f^67s$	1.3223	1.321	1.304	362	$5f^67s$
13,726	13,787	61	$5f^66d$	0.7346	0.784		79	$5f^66d$
16,746	16,903	157	$5f^66d$	1.8794	1.671		81	$5f^66d$
18,666	19,200	534	$5f^66d$	1.4378	1.365		153	$5f^66d$
21,058	20,454	−604	$5f^67s$	1.5922	1.59		78	$5f^66d$
21,542	21,629	87	$5f^66d$	1.5809	1.279		81	$5f^66d$

Table 6. Energy levels and g-factors of J = 3.5 even states.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	g_{obs2}	IS	Conf[expt]
5718	5718	0	$5f^67s$	1.601	1.596	1.579	384	$5f^67s$
9242	9695	452	$5f^67s$	1.386	1.369		373	$5f^67s$
15,488	15,285	−203	$5f^66d$	1.062	1.057		79	$5f^66d$
	18,832		$5f^66d$	1.714				
20,176	20,680	504	$5f^66d$	1.456	1.515		87	$5f^66d$
22,198	22,854	657	$5f^66d$	1.527	1.53		81	$5f^66d$

Table 7. Energy levels and g-factors of J = 4.5 even states.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	IS	Conf[expt]
7279	7279	0	$5f^67s$	1.559	1.545	378	$5f^67s$
10,726	11,278	552	$5f^67s$	1.413	1.391	356	$5f^67s$
17,163	16,735	−429	$5f^66d$	1.212	1.2	79	$5f^66d$
21,291	20,619	−672	$5f^66d$	1.641	1.59	96	$5f^66d$
23,250	22,058	−1192	$5f^66d$	1.452	1.475	81	$5f^66d$

Table 8. Energy levels and g-factors of J = 5.5 even states.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	IS	Conf[expt]
8638	8638	0	$5f^67s$	1.533	1.52	385	$5f^67s$
11,799	12,537	737	$5f^67s$	1.420	1.373	357	$5f^67s$
18,762	18,139	−622	$5f^66d$	1.293	1.28	79	$5f^66d$
	20,833		$5f^67s$	0.739			
22,500	22,171	−330	$5f^66d$	1.599	1.555	84	$5f^66d$

3.3. *Lowest-Energy Odd State Calculations*

A similar check for the lowest odd states has been performed for excitations of the same symmetry of the main configuration. Because the initial DHF potential included $5f^6$ valence electrons, some correction was needed for the energy of $5f$ orbitals via PT, which included many nf excitations.

Close agreement was achieved for $5f^57s^2$ and $5f^56d7s$ states, which are dominant configurations in the states we focus on in the next subsection. The others were also approximately correct and their contribution to these low odd states is not very large, so having agreement for the energies shown in Table 9 is quite satisfactory.

Table 9. CI–PT energies and g-factors of lowest odd single-configuration states: ^{a} the experimental energies, g-factors, and IS taken from [30,33], where proper configuration assignment was made. Single excitations "SE" are taken from $5f^67p$ restricted by $6f$ and $8p$ orbitals. Energy of 2700 cm^{-1} was subtracted compared to even state $5f^67s$ for better alignment of odd states. Relative energy between odd and even states does not play any role since they do not couple. Configurations "Conf." are CI–PT dominant configurations. Note the large uncertainty in the energy of the $5f^7$ state, so we did not try to match this energy accurately.

J	Conf.	Exc. Conf.	E_{CI-PT}	E^a	g_{CI-PT}	g^a	IS ^{a}
2.5	$5f^57s^2$	$5f^4nf7s^2$, n = 6–15	7930	8199	0.353	0.414	896
3.5	$5f^56d7s$	$5f^4nf6d7s$, n = 6–11	8780	8710	0.281	0.308	555
4.5	$5f^5d^2$	$5f^56d7d$	15,650	17,297	0.426	0.494	242
3.5	$5f^7$	$5f^6nf$, n = 6–15	30,000	$14 \pm 8 \times 10^3$	1.974		
0.5	$5f^67p$	SE 6f, 8p	26,310	22,039	−0.1059	0.344	287

3.4. Energy Levels, g-Factors, IS, and Dominant Configurations of the Pu II Odd States

Odd states have interplay of $5f^57s^2$, $5f^56d7s$, and $5f^56d^2$ configurations, but mostly the first two. From the analysis presented in the previous subsection, we included the configurations listed in Table 10 into calculations of low-energy odd states, which are presented in Tables 11–13. The theoretical IS was calculated by a fit that assumes three different IS for the above non-relativistic configurations. The states with different J were allowed to have somewhat different IS. This idea of fit follows from the dominance of the field-shift part of IS, which mostly depends on the wave function near the nucleus, and less on the specific fine-structure component, which is quite proper assumption for high-Z atoms such as Pu I or Pu II. The weights are taken from the configuration expansion. In the CI–PT method, we chose the three dominant non-relativistic configuration to include into the P sector, and the rest into Q. Thus, the resulting weights are obtained only for the three configurations.

Table 10. Set of 12 non-relativistic configurations chosen for odd states.

$6p^65f^57s^2$	$6p^65f^56d7s$	$6p^65f^56d^2$
$6p^65f^56d7d$	$6p^65f^57d7s$	$6p^65f^58s6d$
$5f^4nf7s^2, n = 6..15$	$5f^4nf6d7s, n = 6..11$	

The case of J = 3.5 allows identification of theoretical states up to energy of 23,671 cm^{-1}. There are some possible gaps in the experimental data, so experimental and theoretical IS were compared to understand better where missing levels can be located. For example, the seventh theoretical J = 3.5 level has IS = 846, which corresponds to the $5f^57s^2$ state, but experimental data do not have such a large shift for a large range of energies, so it is either that the theory predicts a too low energy level of the $5f^57s^2$ configuration, or the experimental data do not contain information on this level. Similarly, the theory predicts some levels with a quite low IS for the pure $5f^56d7s$ configuration of 485 and 488. The lowest six experimental levels, on the other hand, are in a very close agreement with theory for both IS and g-factors, which gives assurance of correctness of identification and good theoretical accuracy. It is also notable that the last two levels can have some strong mixing resulting in deviations from the experiment of individual g-factors and agreement for the sum: 2.74 vs. 2.85. The energy differences from experiment dE for many states are about 1000 cm^{-1} consistently for most levels.

In the case of J = 4.5, eight experimental and theoretical levels align well, but some gaps in experimental data appear at the 9th and 11th positions. It was also necessary to exchange the second and third theoretical levels to match experimental g-factors and IS. It is interesting to note that an almost pure $5f^5 6d^2$ configuration appears in the 5th position. In case of J = 5.5 states, the g-factor and IS for the 17,121.64 cm^{-1} was missing and several theoretical levels did not find experimental counterparts.

While the considered low-energy states showed good agreement between theory and experiment, unfortunately, the precision was still limited for higher sates leading to some uncertainty in the classification of experimental levels.

4. Discussion and Conclusions

One important thing to note is that unfortunately the website of Laboratoire Aime-Cotton where actinide energies, g-factors, parametric state assignment, and isotope-shifts could be found (http://web2.lac.u-psud.fr/) is currently down and the data are not available, so we compared our calculations with [26], which are quite consistent with this database for the levels we considered, with small differences in the third decimal place.

The method of CI–PT is quite promising for calculations of properties of low-energy states of multi-valence atoms, such as the 7-valence electron Pu II considered here. Typically, Cowan's code based semi-empirical approaches are used for level classification, and here we demonstrate an alternative approach based on CI–PT. We found a reasonable agreement for many low-energy states for energies and g-factors. We also introduced a method for calculating IS values using a small number of fitting parameters, and also obtain close agreement with experiment. The CI–PT calculation of g-factors and IS served as an aid in level identification. Some closely spaced levels had strong mixing resulting in substantial deviations for g-factors, but this is quite expected.

Looking into the future, the CI–PT approach has the potential for *ab initio* calculations in cases when the energy levels are not available, and hence independent testing of the method is required, which was one goal of this work. In addition, CI–PT, CI-MBPT, CI-all-order, and MBPT methods are the family of relativistic approaches within the MBPT framework based on finite DHF spline calculations, and successful demonstration of the good accuracy of one method can lead to better understanding of the others, with the potential for many applications, especially in the calculations of atomic properties relevant to fundamental symmetry tests, such as the electric-dipole moment (EDM), parity non-conservation (PNC), alpha-constant variation, axion search, etc, not currently implemented in Cowan's code.

Table 11. Energy levels, g-factors, and IS of J = 3.5 odd states, which for pure configurations are assumed 941 for $5f^5 7s^2$, 555 for $5f^5 6d7s$, and 294 for $6d^2$ from fitting IS of the nine lowest experimental states. The number of theoretical levels exceeds the number of available experimental levels, which can be due to missing experimental levels.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	IS_{CI-PT}	IS_{expt}
8709.64	8710	0	$5f^5 6d7s$	0.285	0.308	551	555
11,504.095	10,808	−696	$5f^5 7s^2$	0.846	0.859	895	897
14,295.57	14,975	679	$5f^5 6d7s$	0.777	0.79	547	547
15,641.105	16,525	884	$5f^5 6d7s$	0.998	1.04	551	562
16,499.64	17,824	1324	$5f^5 6d7s$	0.761	0.773	494	510
17,532.945	18,549	1016	$5f^5 6d7s$	1.280	1.238	572	571
	18,927		$5f^5 7s^2$	1.328		846	
18,720.09	19,802	1082	$5f^5 6d7s$	0.863	1.06	507	490
19,277.2	20,671	1393	$5f^5 6d7s$	0.684	0.847	454	457
20,689.1	21,416	727	$5f^5 6d7s$	1.167	1.27	542	543
	22,040		$5f^5 6d7s$	0.927		485	
	22,373		$5f^5 6d7s$	0.8857		488	
	22,834		$5f^5 6d7s$	1.2303		535	
22,652.035	23,366	714	$5f^5 6d7s$	1.1822	1.185	535	539
23,538.65	24,767	1229	$5f^5 6d7s$	1.1069	1.47	530	535
23,671.715	25,336	1665	$5f^5 6d7s$	1.6331	1.38	549	514

Table 12. Energy levels, g-factors, IS of J = 4.5 odd states, which for pure configurations are assumed 896 for $5f^5 7s^2$, 555 for $5f^5 6d7s$, and 220 for $6d^2$ by fitting IS for seven lowest experimental states. The number of theoretical levels exceeds the number of available experimental levels, which can be due to missing experimental levels.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	IS_{CI-PT}	IS_{expt}
10,436.77	10,437	0	$5f^5 6d7s$	0.714	0.724	548	555
13,809.91	14,890	1080	$5f^5 6d7s$	0.618	0.657	541	523
14,476.14	13,423	−1053	$5f^5 7s^2$	1.068	1.06	847	871
16,362.00	16,802	440	$5f^5 6d7s$	1.015	1.05	542	550
17,296.91	17,702	405	$5f^5 6d^2$	0.463	0.494	248	242
19,317.37	18,468	−849	$5f^5 6d7s$	1.145	1.225	547	538
19,466.53	20,562	1095	$5f^5 6d7s$	1.371	1.151	536	517
20,063.65	20,829	765	$5f^5 6d7s$	0.957	1.049	480	484
	21,470		$5f^5 7s^2$	1.329		891	
20,511.95	21,523	1012	$5f^5 6d7s$	1.224	1.31	594	554
	22,516		$5f^5 6d7s$	0.6645		396	
22,799.70	22,790	−10	$5f^5 6d7s$	1.2639	1.33	524	546

Table 13. Energy levels, g-factors, and IS of J = 5.5 odd states. By fitting IS for seven lowest experimental states of J = 4.5 odd states, IS for pure configurations are assumed to be 896 for $5f^5 7s^2$, 555 for $5f^5 6d7s$, and 220 for $6d^2$ and configuration weights are used to calculate IS for states with mixed configurations. The number of theoretical levels exceeds the number of available experimental levels, which can be due to missing experimental levels.

E_{exp}	E_{CI-PT}	dE	Conf.	g_{CI-PT}	g_{obs}	IS_{CI-PT}	IS_{expt}
13,013.69	13,013.685	0	$5f^5 6d7s$	0.948	0.95	549	551
	16,196.525		$5f^5 7s^2$	1.188		849	
17,121.64	18,027.955	906	$5f^5 6d7s$	0.931		549	
	19,309.405		$5f^5 6d7s$	1.088		535	
20,073.84	20,532.265	458	$5f^5 6d^2$	0.770	0.79	245	241
	20,686.985		$5f^5 6d7s$	1.230		548	
22,107.41	22,864.415	757	$5f^5 6d7s$	1.066	1.362	544	554
22,409.03	23,471.675	1063	$5f^5 6d7s$	1.288	1.205	545	541
22,537.27	23,901.485	1364	$5f^5 6d7s$	1.216	1.315	533	548

Funding: This research was funded by DOE under contract No. DE-AC52-06NA25396.

Acknowledgments: The author is grateful to Vladimir Dzuba for making his CI+PT code available for this work.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Miziolek, A.W.; Palleschi, V.; Schechter, I. *Laser-Induced Breakdown Spectroscopy (LIBS) Fundamental and Applications*; Cambridge University Press: Cambridge, UK, 2006.
2. Fichet, P.; Mauchien, P.; Moulin, C. Determination of Impurities in Uranium and Plutonium Dioxides by Laser-Induced Breakdown Spectroscopy. *Appl. Spectrosc.* **1999**, *53*, 1111. [CrossRef]
3. Whitehouse, A.I.; Young, J.; Botheroyd, I.M.; Lawson, S.; Evans, C.P.; Wright, J. Remote material analysis of nuclear power station steam generator tubes by laser-induced breakdown spectroscopy. *Spectrochim. Acta Part B* **2001**, *56*, 821. [CrossRef]
4. Gaona, I.; Serrano, J.; Moros, J.; Laserna, J.J. Evaluation of laser-induced breakdown spectroscopy analysis potentialfor addressing radiological threats from a distance. *Spectrochim. Acta Part B* **2014**, *96*, 12. [CrossRef]
5. Singh, J.P.; Yueh, F.Y.; Zhang, H.; Karney, K.P. A Preliminary Study of the Determination of Uranium, Plutonium and Neptunium by Laser-Induced Breakdown Spectroscopy. *Rec. Res. Dev. Appl. Spectrosc.* **1999**, *2*, 59.
6. Miyabe, M.; Oba, M.; Jung, K.; Iimura, H.; Akaoka, K.; Kato, M.; Otobe, H.; Khumaeni, A.; Wakaida, I. Laser ablation absorption spectroscopy for isotopic analysis ofplutonium: Spectroscopic properties and analytical performance. *Spectrochim. Acta Part B* **2017**, *134*, 42. [CrossRef]

7. Savukov, I.; Safronova, U.I.; Safronova, M.S. Relativistic configuration interaction plus linearized-coupled-cluster calculations of U2+ energies, g factors, transition rates, and lifetimes. *Phys. Rev. A* **2015**, *92*, 052516. [CrossRef]
8. Savukov, I.M. Parametric CI+MBPT calculations of Th I energies and g-factors for even states. *J. Phys. B Atomic Mol. Opt. Phys.* **2017**, *50*, 165001. [CrossRef]
9. Cowan, R.D. *The Theory of Atomic Structure and Spectra*; University of California Press: Berkeley, CA, USA, 1981.
10. Kułaga-Egger, D.; Migdałek, J. Theoretical radiative lifetimes of levels in singly ionized lanthanum. *J. Phys. B Atomic Mol. Opt. Phys.* **2009**, *42*, 185002. [CrossRef]
11. Gamrath, S.; Palmeri, P.; Quinet, P. Calculated osicllator strengths for the strongest lines of compchronological interest in the visible spectrum of singly ionized uranium (U II). *Mon. Not. R. Astron. Soc.* **2018**, *480*, 4754.
12. Savukov, I.M.; Anisimov, P.M. Configuration-interaction many-body perturbation theory for La ii electric-dipole transition probabilities. *Phys. Rev. A* **2019**, *99*, 032507. [CrossRef]
13. Rodrigues, G.C.; Indelicato, P.; Santos, J.P.; Patté, P.; Parente, F. Systematic Calculation of Total Atomic Energies of Ground State Configurations. *Atomic Data Nucl. Data Tables* **2004**, *86*, 117–233. [CrossRef]
14. Noro, T.; Sekiya, M.; Osanai, Y.; Koga, T.; Matsuyama, H. Relativistic correlating basis sets for actinide atoms from 90Th to 103Lr. *J. Comput. Chem.* **2007**, *28*, 2511. [CrossRef] [PubMed]
15. Roos, B.O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. New relativistic ANO basis sets for actinide atoms. *Chem. Phys. Lett.* **2005**, *409*, 295. [CrossRef]
16. Cao, X.Y.; Dolg, M. Theoretical Prediction of the Second to Fourth Actinide Ionization Potentials. *Mol. Phys.* **2003**, *101*, 961–969. [CrossRef]
17. Liu, W.; Küchle, W.; Dolg, M. Ab initio pseudopotential and density-functional all-electron study of ionization and excitation energies of actinide atoms. *Phys. Rev. A* **1998**, *58*, 1103. [CrossRef]
18. Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. Energy-adjusted pseudopotentials for the actinides. *J. Chem. Phys.* **1994**, *100*, 7535. [CrossRef]
19. McNally, J.R., Jr.; Griffin, P.M. Preliminary Classification of the Singly Ionized Plutonium Atom (Pu II). *J. Opt. Soc. Am.* **1959**, *49*, 162–166. [CrossRef]
20. Rollefson, G.K.; Dodgen, H.W. *Report on Spectrographic Analysis Work CK-812*; ACS Publication: Washington, DC, USA, 1943.
21. Bovey, L.; Gerstenkorn, S. Ground State of the First Spectrum of Plutonium (Pu i), from an Analysis of its Atomic Spectrum. *J. Opt. Soc. Am.* **1961**, *51*, 522–525. [CrossRef]
22. Bovey, L.; Ridgeley, A. *The Zeeman Effect of Pu I*; Harwell Rep. A.E.R.E.-R3393; Atomic Energy Research Establishment: Harwell, UK, 1960.
23. Gerstenkorn, S. Étude du plutonium par spectroscopie à haute résolution: Contribution à la classification du spectre d'arc. *Ann. Phys.* **1962**, *7*, 367–404. [CrossRef]
24. Striganov, A.R.; Korostyleva, L.A.; Dontsov, Y.P. The Isotopic Shift in the Spectrum of Plutonium. *Zhur Eksptl I Teoret Fiz To* **1955**, *28*, 480.
25. Korostyleva, L.A. Hypefine and isotopic structure in the spectrum of plutonium. *Opt. Spektrosk.* **1963**, *14*, 177.
26. Blaise, J.; Fred, M.; Gutmacher, R.G. *Argonne National Laboratory Report ANL-83-95*; Argonne National Laboratory: Lemont, IL, USA, 1984; 612p.
27. Rajnak, K.; Fred, M. Correlation of isotope shifts with $|\psi(0)|^2$ for actinide configurations. *J. Opt. Soc. Am.* **1977**, *67*, 1314–1323. [CrossRef]
28. Wilson, M. Ab *Initio* Calculation of Screening Effects on $|\psi(0)|^2$ for Heavy Atoms. *Phys. Rev. A* **1968**, *176*, 58–63. [CrossRef]
29. Dzuba, V.A.; Johnson, W.R.; Safronova, M.S. Calculation of isotope shifts for cesium and francium. *Phys. Rev. A* **2005**, *72*, 022503. [CrossRef]
30. Blaise, J.; Fred, M.S.; Carnall, W.T.; Crosswhite, H.M.; Crosswhite, H. *Measurement and Interpretation of Plutonium Spectra*; Argonne National Laboratory Technical Report CONF-821265-1; Argonne National Laboratory: Lemont, IL, USA, 1982; 28p.
31. Carlson, T.A.; Nestor, C.W., Jr.; Wasserman, N.; McDowell, J.D. Calculated Ionization Potentials for Multiply Charged Ions. *Atomic Data Nucl. Data Tables* **1970**, *2*, 63–99. [CrossRef]
32. Nugent, L.J.; Vander Sluis, K.L. Theoretical Treatment of the Energy Differences between $f^q d^1 s^2$ and $f^{q+1} s^2$ Electron Configurations for Lanthanide and Actinide Atomic Vapors. *J. Opt. Soc. Am.* **1971**, *61*, 1112. [CrossRef]

33. Brewer, L. Energies of the Electronic Configurations of the Singly, Doubly, and Triply Ionized Lanthanides and Actinides. *JOSA* **1971**, *61*, 1666. [CrossRef]
34. Dzuba, V.A.; Berengut, J.C.; Harabati, C.; Flambaum, V.V. Combining configuration interaction with perturbation theory for atoms with a large number of valence electrons. *Phys. Rev. A* **2017**, *95*, 012503. [CrossRef]
35. Dzuba, V.A.; Flambaum, V.V. Exponential Increase of Energy Level Density in Atoms: Th and Th II. *Phys. Rev. Lett.* **2010**, *104*, 213002. [CrossRef]
36. Bauche, J.; Blaise, J.; Fred, M. Ground multiplet of the of the spark spectrum of plutonium. *C. R. Acad. Sci. Paris* **1963**, *256*, 5091–5093.