

Atomic properties of Pb III

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We carry out a systematic study of Pb III properties using a hybrid method that combines configuration interaction and linearized coupled-cluster approaches. The calculations start from a $[\text{Xe}]4f^{14}5d^{10}$ Dirac-Fock potential. Excitation energies and lifetimes of the $6p^2$, $6sns$, $6snp$, and $6snd$ ($n \leq 9$) states are evaluated. Reduced matrix elements, oscillator strengths, and transition rates are determined for allowed electric-dipole transitions including these states. Extensive comparison with other exciting theory and experimental values is carried out. Electric-dipole polarizabilities of the $6s^2 \ ^1S_0$, $6s6p \ ^3P_0$, and $6s6p \ ^3P_1$ states in Pb III and ground state polarizability of Pb^{4+} are reported.

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I. INTRODUCTION

Accurate calculations of atomic properties of heavy atoms and ions is needed for many different applications, including study of fundamental symmetries with heavy atoms [1–4], development of optical atomic clocks [5–8], study of degenerate quantum gases [9], quantum information [10], astrophysics [11], actinide chemistry [12], and many others. Recently, we have developed a theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in atoms with few valence electrons. This method combines the all-order (linearized coupled-cluster) approach currently used in precision calculations of properties of monovalent atoms [13] with the configuration-interaction approach that was applicable for many-electron systems [14]. We have extended this approach to the calculation of the ground and excited state polarizabilities and subsequently evaluated black-body radiation shifts in the frequency standards with Al^+ , B^+ , and In^+ [15]. The BBR shift of the $^1S_0 - ^3P_0$ clock states in these systems is proportional to the difference in the static polarizability of the initial and final clock states since the dynamic contribution was found to be negligible [15].

This work is motivated in part by the recent measurements in Pb III. In 2010, polarizabilities of Pb III and Pb V and ionization energies of Pb II and Pb IV from spectroscopy of high- L Rydberg states of Pb^+ and Pb^{3+} were determined by Hanni *et al.* [16]. The binding energies of high- L Rydberg levels of Pb^+ with $n = 19$ or 20 and $6 \leq L \leq 10$ were measured with resonant excitation Stark ionization spectroscopy (RESIS). The polarizability of the $5d^{10}6s^2 \ ^1S_0$ ground state of Pb III was determined to be $\alpha_0 = 13.62(8)$ a.u. [16]. The ground state polarizability of Pb^{4+} was determined to be $\alpha_0 = 3.61(4)$ a.u. [16]. Transition probabilities for 30 spectral lines, arising from the $(5d^{10}6s)8s, 7p, 5f, 5g$ electronic configurations of Pb III were experimentally determined by Alonso-Medina [17]. The line intensities

were obtained with the target placed in molecular argon at 6 Torr, recorded at a 400 ns delay from the laser pulse, which provides appropriate measurement conditions, and analyzed between 200 and 700 nm [17]. Therefore, Pb^{+2} is an excellent case for the benchmark tests of the theory and experiment. Moreover, recent proposal for the development of the frequency standard with Hg atoms and subsequent need for accurate knowledge of the BBR shift, serves as additional motivation to study a Hg-like ion such as Pb III where high-precision measurement of the ground state polarizability is available [16]. No accurate experimental data for Hg polarizabilities are available at this time to the best of our knowledge.

We start with a review of previous studies of Pb III atomic properties. Most of the earlier studies have focused on the two first transitions, $6s^2 \ ^1S_0 - 6s6p \ ^{1,3}P_1$. Relativistic configuration-interaction oscillator strength calculations with *ab initio* model potential wave functions were presented by Glowacki and Migdalek [18]. Transition energies and oscillator strengths for $6s^2 \ ^1S_0 - 6s6p \ ^3P_1$, 1P_1 transitions in the mercury isoelectronic sequence were evaluated [18]. Measurements and predictions of the $6s6p \ ^{1,3}P_1$ lifetimes in the Hg isoelectronic sequence were reported by Curtis *et al.* [19]. Theoretical values of absolute transition probabilities for 54 lines arising from the $6snp$ configuration of Pb III were obtained by Colón and Alonso-Medina [20]. These values were obtained in intermediate coupling (IC) and using *ab initio* relativistic Hartree-Fock calculations (COWAN code). Core-polarization effects for the $6s^2 \ ^1S_0 - 6s6p \ ^3P_1$, 1P_1 transitions in Hg-like ions were investigated by Chou *et al.* [21]. Relativistic excitation energies and oscillator strengths for the $6s^2 \ ^1S_0 \rightarrow 6s6p \ ^1P_1$, 3P_1 transitions in Hg-like ions were reported by Chou and Huang [22]. The beam-foil technique was used by Pinnington *et al.* [23] to measure the lifetimes of levels in Pb III, Pb IV, Bi III and Bi IV. The lifetime values in Pb III were determined for the low-lying levels ($6s6p \ ^{1,3}P_1$, $6s7s \ ^3S_1$, and $6s6d \ ^3D_J$). Beam-foil intensity decay curves for transitions in the

wavelength range from 900 to 2200 Å were used by Ansbacher *et al.* [24] to derive the lifetimes of the $6s6p\ ^1\ ^3P_1$, $6s6d\ ^1D_2$, $6s7s\ ^3S_0$, and $6p^2\ ^1D_2$ levels of Pb III. Arbitrarily normalized decay curve (ANDC) analyzes was used for the $6s6p$ levels. Good agreement was found for two $6s6p$ levels with a recent calculation in which a polarization model accounts for valence-core correlation [25, 26]. Relativistic CI calculations for the $ns^2\ ^1S_0$ – $nsnp\ ^3P_1$, 1P_1 transitions in the cadmium and mercury isoelectronic sequences was presented by Migdalek and Bojara [25]. Relativistic oscillator strengths and excitation energies for the $ns^2\ ^1S_0$ – $nsnp\ ^3P_1$, 1P_1 transitions in the mercury isoelectronic sequence were evaluated by Migdalek and W. Baylis [26]. The spectroscopic study of a laser-produced lead plasma was reported by Colón *et al.* [27]. Core-polarization effects, oscillator strengths and radiative lifetimes of levels in Pb III were investigated by Alonso-Medina *et al.* [11] using the standard method of least-square fitting from experimental energy levels with the Cowan computer code. Transition probabilities and oscillator strengths of 382 lines with astrophysical interest arising from $5d^96s^26p$, $5d^{10}6snl$, $5d^{10}6s^2$, $5d^{10}6s^2$, $5d^{10}6p^2$, $5d^{10}6p7s$, and $5d^{10}6p6d$ configurations and some levels radiative lifetimes of Pb III were calculated. These values were obtained in intermediate coupling (IC) and using relativistic Hartree-Fock calculations including core-polarization effects. The $5d$ photoabsorption spectra of Pb III were investigated by Banahan *et al.* [28]. The photoabsorption spectra of lead ion were recorded using the dual laser plasma (DLP) technique in the photon energy range 30-66 eV. The experimental observations and theoretical calculations were focused on the $5d$ inner-shell excitations of the Hg I like ions of lead (Pb III) and bismuth (Bi IV). Authors underlined that they identified over 30 new lines with the aid of Hartree-Fock calculations in the jj coupling scheme [28]. Determination of polarizabilities and lifetimes for the Mg, Zn, Cd and Hg isoelectronic sequences was reported recently by Reshetnikov *et al.* [29]. Authors considered the systems with a ground state $ns^2\ ^1S_0$ when the total oscillator strength is dominated by the unbranched intrashell $ns^2\ ^1S_0$ – $nsnp\ ^1P_1$ transition, and the remaining oscillator strength can be narrowly bracketed using the f -sum rule. Authors concluded that measurements of the lifetime of the lowest resonance transition can be used to specify the polarizabilities and, alternatively, measurements of the polarizabilities can be used to deduce lifetimes [29].

In present paper, we evaluate the atomic properties of Pb III using the CI+all-order approach. The energies, oscillator strengths, transition rates, and lifetime of low-lying levels are evaluated and compared with available experimental and theoretical results. Polarizabilities of the $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ states are reported.

TABLE I: Comparison of the CI + all-order results for the energy levels of Pb III with experimental energies E_{NIST} [30, 31]. The ionization energy of Pb^{3+} was taken from [16]. Two-electron binding energies are given in the first row of Table I, energies in other rows are counted from the ground state. The energies are given in cm^{-1} and the relative differences with experimental values are given in the last column in percent.

Level	Expt.	Present	Δ (%)
$6s^2\ ^1S_0$	598942	600984	-0.33
$6s6p\ ^3P_0$	60397	61283	-1.47
$6s6p\ ^3P_1$	64391	65089	-1.08
$6s6p\ ^3P_2$	78985	80029	-1.32
$6s6p\ ^1P_1$	95340	95847	-0.53
$6p^2\ ^3P_0$	142551	143571	-0.72
$6s7s\ ^3S_1$	150084	151183	-0.73
$6s6d\ ^1D_2$	151885	153614	-1.14
$6s7s\ ^1S_0$	153783	155054	-0.83
$6p^2\ ^3P_1$	155431	156610	-0.76
$6s6d\ ^3D_1$	157444	158439	-0.63
$6s6d\ ^3D_2$	157925	159134	-0.77
$6s6d\ ^3D_3$	158957	160530	-0.99
$6p^2\ ^3P_2$	164818	165898	-0.66
$6s7p\ ^3P_0$	170917	172026	-0.65
$6s7p\ ^3P_1$	171081	172460	-0.81
$6s7p\ ^3P_2$	176023	176732	-0.40
$6s7p\ ^1P_1$	177181	178172	-0.56
$6p^2\ ^1D_2$	178432	179646	-0.68
$6p^2\ ^1S_0$	188615	190061	-0.77
$6s5f\ ^3F_3$	189785	190451	-0.35
$6s5f\ ^3F_2$	190288	190560	-0.14
$6s5f\ ^3F_4$	190429	190552	-0.06
$6s5f\ ^1F_3$	190901	191699	-0.42
$6s8s\ ^3S_1$	197893	198814	-0.47
$6s8s\ ^1S_0$	199401	200428	-0.52
$6s7d\ ^3D_1$	201399	202379	-0.49
$6s7d\ ^3D_2$	201597	202617	-0.51
$6s7d\ ^3D_3$	202047	203230	-0.59
$6s7d\ ^1D_2$	203302	204392	-0.54
$6s8p\ ^3P_0$	206809	207645	-0.40
$6s8p\ ^3P_1$	206979	207782	-0.39
$6s8p\ ^3P_2$	208922	209759	-0.40
$6s8p\ ^1P_1$	209318	210063	-0.36
$6s6f\ ^3F_2$	214434	214993	-0.26
$6s6f\ ^3F_3$	214477	214965	-0.23
$6s6f\ ^3F_4$	214486	215054	-0.26
$6s6f\ ^1F_3$	214846	215636	-0.37
$6s9s\ ^3S_1$	219910	220228	-0.14
$6s8d\ ^3D_1$	221205	222085	-0.40
$6s8d\ ^3D_2$	221307	222188	-0.40
$6s8d\ ^3D_3$	221600	222483	-0.40
$6s8d\ ^1D_2$	221935	222848	-0.41

II. EXCITATION ENERGIES IN PB III

In the CI + all-order approach introduced in [14], corrections to the effective Hamiltonian Σ_1 and Σ_2 are calculated using a modified version of the linearized coupled-cluster method with single and double excita-

TABLE II: Comparison of the CI + all-order results for the oscillator strengths f and transition rates (A_r in 10^7 s^{-1}) of Pb III with theoretical results given by Alonso-Medina *et al.* [11]. Numbers in brackets represent powers of 10.

Levels		λ (in Å)	f	f	A_r	A_r	Levels		λ (in Å)	f	f	A_r	A_r
Lower	Upper	[30, 31]	Present	[11]	Present	[11]	Lower	Upper	[30, 31]	Present	[11]	Present	[11]
$6s^2 \ ^1S_0$	$6s7p \ ^3P_1$	584.5	5.39[-3]	6.45[-3]	3.51	4.2	$6s6p \ ^3P_0$	$6s8s \ ^3S_1$	727.3	2.22[-2]	4.00[-2]	9.35	16.8
$6s6p \ ^1P_1$	$6s9s \ ^1S_0$	802.5	1.26[-2]	1.18[-2]	39.1	36.8	$6s6p \ ^3P_1$	$6s8s \ ^3S_1$	749.1	2.27[-2]	3.61[-2]	26.9	42.9
$6s6p \ ^3P_2$	$6s8s \ ^3S_1$	841.0	2.87[-2]	3.58[-2]	45.1	56.3	$6s6p \ ^1P_1$	$6s8s \ ^3S_1$	975.1	1.68[-3]	2.70[-3]	1.18	1.9
$6s6p \ ^3P_1$	$6p^2 \ ^3P_2$	995.7	2.12[-1]	2.53[-1]	85.6	102	$6s6p \ ^3P_0$	$6s6d \ ^3D_1$	1030.4	6.78[-1]	9.30[-1]	142	194
$6s6p \ ^3P_2$	$6p^2 \ ^1D_2$	1005.6	1.58[-1]	1.26[-1]	104	50.0	$6s6p \ ^3P_0$	$6p^2 \ ^3P_1$	1052.2	6.91[-1]	4.30[-1]	139	86.6
$6s^2 \ ^1S_0$	$6s6p \ ^1P_1$	1048.9	1.65[0]	1.24[0]	333	252	$6s6p \ ^1P_1$	$6p^2 \ ^1S_0$	1072.1	1.93[-1]	3.34[-1]	337	258
$6s6p \ ^3P_1$	$6s6d \ ^3D_2$	1069.1	7.36[-1]	6.91[-1]	258	242	$6s6p \ ^3P_1$	$6p^2 \ ^3P_1$	1098.4	6.36[-2]	9.60[-2]	35.2	53.0
$6s6p \ ^3P_1$	$6s6d \ ^3D_1$	1074.7	2.38[-1]	2.08[-1]	137	120	$6s6p \ ^3P_1$	$6p^2 \ ^3P_0$	1279.4	1.67[-1]	1.13[-1]	204	138
$6s6p \ ^3P_0$	$6s7s \ ^3S_1$	1115.0	2.53[-1]	2.29[-1]	45.2	41.0	$6s6p \ ^3P_2$	$6p^2 \ ^3P_1$	1308.1	1.53[-1]	8.72[-2]	99.7	56.7
$6s6p \ ^3P_2$	$6p^2 \ ^3P_2$	1165.0	2.66[-1]	2.10[-1]	131	103	$6s6p \ ^1P_1$	$6p^2 \ ^3P_2$	1439.3	4.99[-1]	2.77[-1]	96.5	53.5
$6s6p \ ^3P_1$	$6s7s \ ^3S_1$	1167.0	1.91[-1]	2.04[-1]	93.8	100	$6s6p \ ^1P_1$	$6s6d \ ^3D_2$	1597.8	1.71[-2]	2.87[-2]	2.68	3.7
$6s6p \ ^1P_1$	$6p^2 \ ^1D_2$	1203.5	1.08[0]	1.12[0]	299	310	$6s6p \ ^1P_1$	$6s6d \ ^3D_1$	1610.2	2.04[-2]	1.20[-2]	5.25	3.1
$6s6p \ ^3P_2$	$6s6d \ ^3D_3$	1250.4	7.75[-1]	6.42[-1]	236	196	$6s6d \ ^3D_1$	$6s6f \ ^3F_2$	1754.7	7.58[-3]	1.08[-2]	0.99	1.4
$6s6p \ ^3P_2$	$6s6d \ ^3D_2$	1266.8	8.83[-2]	9.00[-2]	36.7	37.5	$6s6d \ ^3D_2$	$6s6f \ ^3F_3$	1768.3	5.82[-3]	9.19[-3]	0.89	1.4
$6s6p \ ^3P_2$	$6s6d \ ^1D_2$	1371.7	5.35[-2]	4.26[-2]	19.0	15.1	$6p^2 \ ^3P_2$	$6s6f \ ^1F_3$	1998.9	2.15[-2]	1.26[-2]	2.56	1.5
$6s6p \ ^3P_2$	$6s7s \ ^3S_1$	1406.5	1.68[-1]	1.82[-1]	94.6	102	$6s7p \ ^3P_1$	$6s9s \ ^1S_0$	2048.7	7.84[-3]	1.26[-2]	3.74	6.0
$6s^2 \ ^1S_0$	$6s6p \ ^3P_1$	1553.0	8.11[-2]	7.40[-2]	7.47	6.9	$6s7p \ ^1P_1$	$6s9s \ ^1S_0$	2340.3	3.04[-2]	1.55[-2]	11.1	5.7
$6s6p \ ^1P_1$	$6s7s \ ^3S_1$	1711.1	1.57[-1]	1.52[-1]	107	104	$6s6d \ ^1D_2$	$6s5f \ ^1F_3$	2563.0	5.61[-1]	2.95[-1]	40.7	21.4
$6s6p \ ^1P_1$	$6s6d \ ^1D_2$	1768.5	1.37[-2]	1.25[-2]	1.75	1.6	$6s8p \ ^3P_1$	$6s9s \ ^1S_0$	7733.3	8.23[-2]	1.61[-1]	2.75	5.4
$6s6d \ ^3D_3$	$6s6f \ ^3F_4$	1800.9	8.45[-3]	9.38[-3]	1.35	1.5							
$6s6d \ ^3D_2$	$6s5f \ ^3F_2$	3090.0	9.61[-2]	1.13[-1]	6.7	7.9	$6s^2 \ ^1S_0$	$6s7p \ ^1P_1$	564.4	5.32[-3]	1.96[-2]	3.71	13.7
$6s6d \ ^3D_3$	$6s5f \ ^3F_3$	3243.8	6.82[-2]	7.57[-2]	4.32	4.8	$6s6p \ ^3P_1$	$6s9s \ ^1S_0$	643.0	4.79[-4]	1.11[-3]	2.32	5.4
$6s6d \ ^3D_1$	$6s7p \ ^3P_1$	7332.8	6.34[-2]	7.74[-2]	0.79	0.96	$6s6p \ ^3P_1$	$6s8s \ ^1S_0$	740.7	7.48[-4]	1.54[-3]	2.73	5.6
$6s6d \ ^3D_1$	$6s7p \ ^3P_0$	7422.1	1.14[-1]	1.31[-1]	4.15	4.8	$6s6p \ ^3P_1$	$6p^2 \ ^1S_0$	805.0	3.16[-3]	1.39[-3]	9.76	4.3
$6s6d \ ^3D_2$	$6s7p \ ^3P_1$	7600.9	1.25[-1]	1.30[-1]	2.41	2.5	$6s6p \ ^1P_1$	$6s8s \ ^1S_0$	961.0	5.51[-2]	2.39[-2]	119	51.9
$6s7d \ ^3D_1$	$6s6f \ ^3F_2$	7671.5	1.38[0]	1.44[0]	9.37	9.8	$6s6p \ ^3P_1$	$6s7s \ ^1S_0$	1118.7	8.63[-3]	3.27[-2]	13.8	52.3
$6s7d \ ^3D_2$	$6s6f \ ^3F_3$	7764.2	1.06[0]	1.21[0]	8.39	9.6	$6s6p \ ^3P_1$	$6s6d \ ^1D_2$	1142.9	1.91[-2]	2.42[-3]	5.85	0.7
$6s7d \ ^3D_2$	$6s6f \ ^3F_2$	7790.2	1.44[-1]	1.46[-1]	1.58	1.6	$6s6p \ ^3P_2$	$6s6d \ ^3D_1$	1274.5	2.15[-2]	7.44[-3]	14.7	5.1
$6s7d \ ^3D_3$	$6s6f \ ^3F_4$	8039.1	1.28[0]	1.25[0]	10.3	10.0	$6s6p \ ^1P_1$	$6p^2 \ ^3P_1$	1664.1	1.78[-3]	5.40[-3]	0.43	1.3
$6s7d \ ^3D_3$	$6s6f \ ^3F_3$	8044.9	1.08[-1]	1.07[-1]	1.11	1.1	$6s6p \ ^1P_1$	$6s7s \ ^3S_1$	1826.7	2.26[-2]	1.10[-2]	4.52	2.2
$6s7d \ ^1D_2$	$6s6f \ ^1F_3$	8662.2	1.11[0]	1.39[0]	7.02	8.8	$6s6p \ ^1P_1$	$6p^2 \ ^3P_0$	2118.2	1.97[-3]	2.91[-5]	0.88	0.013
$6s8p \ ^1P_1$	$6s9s \ ^1S_0$	9441.1	3.33[-1]	2.94[-1]	7.47	6.6	$6s7d \ ^3D_2$	$6s6f \ ^1F_3$	7547.9	1.81[-1]	5.14[-2]	1.51	0.43
							$6s6d \ ^1D_2$	$6s6f \ ^1F_3$	8158.3	1.13[-2]	4.45[-2]	2.13	8.4

tions (LCCSD) all-order method described in [32, 33]. Therefore, the effective Hamiltonian contains dominant core and core-valence correlation corrections to all orders. The core-core and core-valence sectors of the correlation corrections for systems with few valence electrons are treated in the all order method with the same accuracy as in the all-order approach for the monovalent systems. The CI method is then used to treat valence-valence correlations [34].

The CI + all-order approach is based on the Brillouin-Wigner variant of the many-body perturbation theory, rather than the Rayleigh-Schrödinger variant. In the present implementation, the $\tilde{\epsilon}_v$ one-particle energy is introduced in the denominators as described in [14]. When $\tilde{\epsilon}_v$ is taken to be equal to the Dirac-Fork energy of the corresponding orbital, the formulas coincide with the original implementation of the LCCSD method [13] based on the Rayleigh-Schrödinger variant (with terms included in the CI subtracted out). However, the use of the Rayleigh-

Schrodinger MBPT for systems with more than one valence electron leads to a nonsymmetrical effective Hamiltonian and to the problem of “intruder states.” In the Brillouin-Wigner variant of MBPT, the effective Hamiltonian is symmetric and accidentally small denominators do not arise; however, Σ_1 and Σ_2 became energy dependent leading to the introduction of the $\tilde{\epsilon}_v$ parameter in the practical implementation of the method. We refer the reader to Ref. [14] for the formulas and detail description of the CI + all-order method. In this work, we follow the prescription of [14] and take $\tilde{\epsilon}_v$ to be the DF energy of the lowest valence state for each partial wave. For example, DF energy of the $6s$ state is taken to be $\tilde{\epsilon}$ for all of the ns orbitals.

We compare the results of our CI + all-order *ab initio* calculations for the two-electron excitation energies of the Hg-like Pb III ion with experiment in Table I. Two-electron binding energies are given in the first row of Table I, energies in other rows are counted from the

TABLE III: Comparison of the CI + all-order results for the oscillator strengths f and transition rates (in 10^7 s^{-1}) of Pb III with theoretical results given by Alonso-Medina *et al.* [11] and experimental measurements by Alonso-Medina [17]. Numbers in brackets represent powers of 10.

Levels		λ (in Å) [30, 31]	Oscillator Strengths		Transition rates (in 10^7 s^{-1})		
Lower	Upper		Present	[11]	Present	[11]	[17]
$6s6d \ ^3D_1$	$6s5f \ ^3F_2$	3044.7	8.76[-1]	1.05[0]	37.8	45.3	36.8±3.8
$6s6d \ ^3D_2$	$6s5f \ ^3F_3$	3138.7	7.63[-1]	8.64[-1]	36.9	41.8	34.2±3.6
$6s6d \ ^3D_3$	$6s5f \ ^3F_4$	3177.4	8.46[-1]	9.34[-1]	43.5	48.0	39.6±4.0
$6s7s \ ^3S_1$	$6s7p \ ^1P_1$	3690.4	9.81[-2]	1.25[-1]	4.80	6.1	7.0±0.75
$6s7p \ ^3P_0$	$6s8s \ ^3S_1$	3707.1	2.70[-1]	3.71[-1]	4.37	6.0	6.9±0.8
$6s7p \ ^3P_1$	$6s8s \ ^3S_1$	3729.8	2.26[-1]	2.77[-1]	10.8	13.3	14.3±1.5
$6s7s \ ^3S_1$	$6s7p \ ^3P_2$	3855.2	8.45[-1]	6.68[-1]	22.8	18.0	20.8±2.1
$6s7s \ ^3S_1$	$6s7p \ ^3P_1$	4762.4	3.45[-1]	3.43[-1]	10.2	10.1	10.3±1.0
$6s7s \ ^3S_1$	$6s7p \ ^3P_0$	4799.9	1.44[-1]	1.47[-1]	12.5	12.8	15.7±1.7
$6s7p \ ^1P_1$	$6s8s \ ^3S_1$	4828.3	7.19[-2]	5.94[-2]	2.06	1.7	2.0±0.3
$6s6d \ ^3D_2$	$6s7p \ ^3P_2$	5525.5	6.05[-2]	4.57[-2]	1.32	1.0	4.5±0.45
$6s7s \ ^1S_0$	$6s7p \ ^3P_1$	5781.0	2.16[-1]	1.80[-1]	1.44	1.2	9.2±1.0
$6s6d \ ^3D_3$	$6s7p \ ^3P_2$	5859.6	2.49[-1]	2.21[-1]	6.77	6.0	6.9±0.72
$6s7p \ ^3P_1$	$6s8s \ ^1S_0$	3531.2	4.56[-2]	6.54[-2]	7.31	10.5	11.0±1.2
$6s7p \ ^3P_2$	$6s8s \ ^3S_1$	4572.5	3.40[-1]	2.14[-1]	18.1	11.4	13.1±1.4
$6s6d \ ^3D_1$	$6s7p \ ^1P_1$	5066.5	1.88[-2]	3.12[-2]	0.49	0.81	0.91±0.15
$6s6d \ ^3D_2$	$6s7p \ ^1P_1$	5193.1	2.87[-2]	5.09[-2]	1.18	2.1	2.5±0.35
$6s6d \ ^1D_2$	$6s7p \ ^1P_1$	3953.1	1.16[-1]	1.04[-2]	8.23	0.74	0.88±0.095
$6s6d \ ^1D_2$	$6s7p \ ^3P_2$	4142.8	1.24[-4]	3.86[-4]	4.8[-3]	1.5[-2]	0.93±0.15
$6s7s \ ^1S_0$	$6s7p \ ^1P_1$	4273.9	1.13[0]	3.45[-1]	13.7	4.2	4.8±0.55
$6s7p \ ^1P_1$	$6s8s \ ^1S_0$	4500.6	2.54[-1]	7.19[-2]	25.1	7.1	8.7±1.0
$6p^2 \ ^3P_1$	$6s7p \ ^3P_2$	4856.4	1.18[-2]	5.31[-6]	0.20	1[-4]	0.86±0.095
$6s6d \ ^1D_2$	$6s7p \ ^3P_1$	5209.2	3.48[-2]	1.41[-2]	1.43	0.59	2.7±0.3
$6s6d \ ^3D_1$	$6s7p \ ^3P_2$	5382.5	8.66[-3]	1.81[-2]	0.12	0.25	0.26±0.035

ground state. The energies are given in cm^{-1} and the relative differences with experimental values are given in the last column in percentages. The difference is about 1%. While we only list CI+all-order energies, we also carried calculations in the CI+MBPT approach. We also observed significant improvement in the precision of the energy levels with CI+all-order method in comparison with the CI+MBPT one. Further discussion of the accuracy of CI+all-order approach and comparison of the CI+all-order and CI+MBPT values is given in Section V.

III. OSCILLATOR STRENGTHS, TRANSITION RATES, AND LIFETIMES IN PB III

Our CI + all-order results for the oscillator strengths f and transition rates A_r in Pb III are listed in Tables II and III. We evaluate the electric-dipole matrix elements for transitions between the levels given in Table I. Our CI + all-order values are compared with recent theoretical results given by Alonso-Medina *et al.* [11] and experimental measurements by Alonso-Medina [17]. We use NIST compilation of energies [30, 31] to evaluate the f and A_r values for the convenience of comparison since the NIST energies were also used in Ref. [11]. In [11], the f and A_r values were obtained in intermediate coupling

(IC) using relativistic Hartree-Fock calculations including core-polarization effects implemented by COWAN code with the standard method of least-square fitting from experimental energy levels [11]. We find that the agreement between two theoretical approaches is better for the strong transitions. It is expected since the properties of weaker transitions are generally more sensitive to different treatment of the relativistic and correlation correction. Our calculations of the matrix elements include the correlation in a rather complete and consistent way and contain no semi-empirical adjustments.

For convenience, we ordered the transitions in Table II by the level of the agreement between the two calculations. The left part of Table II includes transitions with the smallest (less than 25%) differences between our CI + all-order results (column “Present”) and results obtained by Alonso-Medina *et al.* [11]. The first nineteen lines in the right part of Table II include transitions that differ by less than a factor of two, but more than 25%. The last thirteen transitions are transitions with the largest differences between our results and results from Ref. [11]. Almost all transitions displayed in the left part of Table II are transitions with $\Delta S = 0$, while the most of the transitions displayed in the right part of Table II are transitions with $\Delta S = 1$. The numerical values of oscillator strengths and transitions rates listed in the left

TABLE IV: Comparison of the Pb III lifetimes (in nsec) with other theoretical results from Alonso-Medina *et al.* [11] and experimental measurements by Pinnington *et al.* [23] and by Ansbacher *et al.* [24]. Uncertainties are given in parenthesis. References are given in square brackets. We use energies from E_{NIST} [30, 31].

Level	Energy [30, 31]	Lifetimes (in nsec)		
		Present	[11]	Expt.
$6s6p\ ^3P_1$	64391.0	13.38	14.4	14.8(1.0)[23]
$6s6p\ ^1P_1$	95340.1	0.301	0.40	0.380 (10)[23]
$6p^2\ ^3P_0$	142551.0	0.487	0.72	
$6s7s\ ^3S_1$	150083.7	0.420	0.41	0.47(5)[23]
$6s6d\ ^1D_2$	151884.5	3.764	5.7	6.1(4)[24]
$6s7s\ ^1S_0$	153783.4	0.824	0.64	0.89(5)[24]
$6p^2\ ^3P_1$	155431.5	0.365	0.51	
$6s6d\ ^3D_1$	157444.1	0.334	0.31	
$6s6d\ ^3D_2$	157925.0	0.337	0.36	0.35(3)[23]
$6s6d\ ^3D_3$	158956.8	0.423	0.51	0.49(5)[23]
$6p^2\ ^3P_2$	164817.9	0.320	0.39	
$6s7p\ ^3P_0$	170917.3	6.014	5.68	
$6s7p\ ^3P_1$	171081.4	5.011	5.12	
$6s7p\ ^3P_2$	176022.9	3.206	3.94	
$6s7p\ ^1P_1$	177181.4	2.980	3.59	
$6p^2\ ^1D_2$	178432.0	0.247	0.27	0.51(3)[23]
$6p^2\ ^1S_0$	188615.0	0.288	0.38	
$6s5f\ ^3F_3$	189785.2	2.383		
$6s5f\ ^3F_2$	190287.8	2.193		
$6s5f\ ^3F_4$	190429.	2.301		
$6s5f\ ^1F_3$	190901.2	1.957		
$6s8s\ ^3S_1$	197892.8	0.848	0.65	
$6s8s\ ^1S_0$	199400.6	0.647	1.08	
$6s7d\ ^3D_1$	201398.7	0.972		
$6s7d\ ^3D_2$	201597.3	0.996		
$6s7d\ ^3D_3$	202046.8	1.305		
$6s7d\ ^1D_2$	203301.6	0.939		
$6s8p\ ^3P_0$	206809.	20.55		
$6s8p\ ^3P_1$	206809.	10.36		
$6s8p\ ^3P_2$	208922.	9.802		
$6s8p\ ^1P_1$	209318.	7.041		
$6s6f\ ^3F_2$	214434.	7.995		
$6s6f\ ^3F_3$	214477.	7.829		
$6s6f\ ^3F_4$	214486.	8.598		
$6s6f\ ^1F_3$	214846.	5.512		
$6s9s\ ^3S_1$	219344.	1.414	1.51	
$6s9s\ ^1S_0$	219910.	1.400	1.26	

part of Table II are larger by a factor of 10-100 than the numerical values of f and A_r listed in the right part of Table II. The larger discrepancy for smallest and largest values of f and A_r results, obtained by different methods was discussed in numerous papers (see, for example, Refs. [35–40]). The transitions with $\Delta S = 1$ are particularly sensitive to different treatment of relativistic corrections.

We noticed some inconsistencies in f and A_r values given in Ref. [11] and listed in Table II. For example, the f and A_r values are equal to 0.126 and $50.0 \times 10^7 \text{ s}^{-1}$ for the $6s6p\ ^3P_2 - 6p^2\ ^1D_2$ transition with $\lambda = 1005.6 \text{ \AA}$. Us-

ing $f = 0.126$ and $\lambda = 1005.6 \text{ \AA}$, we find $A_r = 82.9$ instead of 50.0 in units 10^7 s^{-1} . We found similar inconsistencies in f and A_r values for the $6s6p\ ^1P_1 - 6p^2\ ^1S_0$ and $6s6p\ ^1P_1 - 6p^2\ ^3D_2$ transitions with $\lambda = 1072.1 \text{ \AA}$ and $\lambda = 1597.8 \text{ \AA}$, respectively.

We include experimental values for the transition rates obtained by Alonso-Medina [17] in the last column of Table III. The f and A_r results in this table are also divided into three parts by the level of agreement between our results and theoretical results in Refs. [11, 17]. The differences in results listed in the first 13 lines are less than 25%, while the the differences in results listed in the next four lines larger than 25% but smaller than a factor of two. The differences in results listed in the last seven lines are larger than a factor of two. In Table 4 of Ref. [17], authors made comparison of their new measurements with previous measurements [27] and theoretical results [11, 20]. In some cases, they show the disagreement by an order of magnitude. As a result, the comparison with experimental values is inconclusive. In about half of the cases, our values are in better agreement with the experiential measurements, while Alonso-Medina *et al.* [11, 20] values are in better agreement with the other half. Further experimental measurements of transition rates between low-lying states would be extremely helpful in benchmark testing of the theoretical methodologies.

Our lifetime values are compared with theoretical results by Alonso-Medina *et al.* [11] and experimental measurements by Pinnington *et al.* [23] and by Ansbacher *et al.* [24] in Table IV. The accuracy of the CI+all-order matrix elements (and consequently transition rates and lifetimes) is given in Section V.

IV. POLARIZABILITIES OF THE $6s^2\ ^1S_0$, $6s6p\ ^3P_0$, AND $6s6p\ ^3P_1$ STATES

The Pb^{+2} scalar polarizability, α_0 , may be separated into a ionic core polarizability, a core modification due to the valence electron, (term VC), and a valence polarizability. The ionic core polarizability is the ground state polarizability of Pb^{4+} , which we evaluated in the random-phase approximation (RPA), an approach that is expected to provide core values accurate to better than 5% [41]. The core polarizability is corrected for Pauli blocking of core-valence excitations by introducing an extra term VC. We approximate this terms by adding VC contributions from the individual electrons, i.e. $\alpha_{vc}(6s^2) = 2 \times \alpha_{vc}(6s)$, and $\alpha_{vc}(6s6p) = \alpha_{vc}(6s) + \alpha_{vc}(6p)$. For consistency, this term is also calculated in RPA. We note that VC contributions are small.

The valence polarizability is determined by solving the inhomogeneous equation of perturbation theory in the valence space, which is approximated as

$$(E_v - H_{\text{eff}})|\Psi(v, M')\rangle = D_{\text{eff},q}|\Psi_0(v, J, M)\rangle \quad (1)$$

for a state v with the total angular momentum J and

TABLE V: Contributions to the $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ polarizabilities α_0 in a_0^3 . Absolute values of the corresponding reduced electric-dipole matrix elements are listed in column labeled “ D ”. The values a_0^a and a_0^b are calculated with CI + all-order energies and NIST energies, respectively. The matrix elements are from CI+all-order calculations in both cases. Final polarizability values are listed in rows labeled “Total”. Our core value, i.e. Pb4+ polarizability, is compared with the experimental measurement.

Level	Contr	D	α_0^a	α_0^b	
$6s^2\ ^1S_0$	$6s6p\ ^1P_1$	-2.384	8.6784	8.7245	
	$6s7p\ ^1P_1$	0.099	0.0081	0.0082	
	$6s8p\ ^1P_1$	-0.005	0.0000	0.0000	
	$6s9p\ ^1P_1$	-0.060	0.0023	0.0023	
	$6s6p\ ^3P_1$	0.644	0.9317	0.9418	
	$6s7p\ ^3P_1$	0.102	0.0088	0.0089	
	$6s8p\ ^3P_1$	-0.076	0.0041	0.0041	
	$6s9p\ ^3P_1$	-0.016	0.0002	0.0002	
	Sum		9.6336	9.6899	
	Other		0.0418	0.0418	
	Core, Th.		3.629	3.629	
	Core, Expt. [16]			3.61(4)	
	VC		-0.062	-0.062	
	Total		13.24	13.30	
	Expt.[16]			13.62(8)	
	$6s6p\ ^3P_0$	$6p^2\ ^3P_1$	1.548	3.6757	3.6870
		$6s6d\ ^3D_1$	-1.516	3.4616	3.4655
$6s7d\ ^3D_1$		0.444	0.2043	0.2044	
$6s8d\ ^3D_1$		0.228	0.0471	0.0471	
$6s7s\ ^3S_1$		0.963	1.5101	1.5136	
$6s8s\ ^3S_1$		-0.231	0.0567	0.0567	
$6s9s\ ^3S_1$		-0.136	0.0170	0.0169	
$6s10s\ ^3S_1$		-0.094	0.0075	0.0075	
Sum			8.9799	8.9988	
Other			0.1511	0.1511	
Core			3.629	3.629	
VC			-0.240	-0.240	
Total			12.52	12.54	

projection M [42]. The wave function $\Psi(v, M')$, where $M' = M + q$, is composed of parts that have angular momenta of $J' = J, J \pm 1$ from which the scalar and tensor polarizability of the state $|v, J, M\rangle$ can be determined [42]. The construction of the effective Hamiltonian H_{eff} using the all-order approach is described in [14]. The effective dipole operator D_{eff} includes random phase approximation (RPA) corrections. The calculations are carried out with a finite B-spline basis set [43], with several lower orbitals replaced by exact Dirac-Hartree-Fock (DHF) functions [44].

The breakdown of the contributions to the $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ polarizabilities α_0 of Pb III in a_0^3 is given in Table V. Absolute values of the corresponding reduced electric-dipole matrix elements are listed in column labeled “ D ” in a_0e . It is useful to establish which terms give the dominant contributions. If one or a few terms are dominant, their accuracy may be improved if corresponding E1 matrix elements were measured to high precision.

TABLE VI: Contributions to the $6s6p\ ^3P_1$ polarizabilities α_0 in a_0^3 . Absolute values of the corresponding reduced electric-dipole matrix elements are listed in column labeled “ D ”. The “Other” contribution is estimated from data for the $6s6p\ ^3P_0$ level. Final polarizability value is listed in row labeled “Total”.

Level	Contr	D	α_0
$6s6p\ ^3P_1$	$6s6d\ ^3D_2$	2.788	4.053
	$6s7d\ ^3D_2$	0.686	0.167
	$6s8d\ ^3D_2$	0.354	0.039
	$6s7s\ ^3S_1$	1.486	1.256
	$6s8s\ ^3S_1$	-0.409	0.061
	$6s9s\ ^3S_1$	-0.237	0.018
	$6s10s\ ^3S_1$	-0.163	0.008
	$6s6d\ ^3D_1$	1.590	1.325
	$6s7d\ ^3D_1$	-0.368	0.048
	$6s8d\ ^3D_1$	-0.184	0.010
	$6s^2\ ^1S_0$	0.644	-0.314
	$6p^2\ ^3P_0$	1.454	1.319
	$6p^2\ ^1S_0$	0.159	0.010
	$6p^2\ ^3P_1$	0.831	0.370
	$6p^2\ ^3P_2$	-1.445	1.013
	$6p^2\ ^1D_2$	-0.080	0.003
	$6s6d\ ^1D_2$	-0.464	0.120
	$6s7d\ ^1D_2$	0.117	0.005
	$6s8d\ ^1D_2$	-0.042	0.001
	$6s7s\ ^1S_0$	0.309	0.052
	$6s8s\ ^1S_0$	-0.074	0.002
	$6s9s\ ^1S_0$	-0.055	0.001
	$6s10s\ ^1S_0$	-0.039	0.000
	$6s11s\ ^1S_0$	-0.029	0.000
	Sum		9.567
	Other		0.163
	Core		3.629
	VC		-0.221
	Total		13.13

We separately calculated several dominant contributions to polarizabilities by combining our values of the E1 matrix elements and energies as $2D_{gn}^2/3\Delta E_{gn}$ according to the sum-over-states formula [45] with $J_g=0$. We used both *ab initio* CI+all-order and NIST experimental energies when evaluating sum-over-state terms. These results are listed in columns labelled $\alpha_0^{(a)}$ and $\alpha_0^{(b)}$, respectively. The differences between these results are small since the theoretical energies are in good agreement with experimental values. In the case of the transitions from the $6s6p$ states, the accuracy of our transition energies is substantially better than the accuracy of the energy levels. For example, CI+all-order transition energies for three transitions that are dominant for $6s6p\ ^3P_0$ polarizability are accurate to 0.1-0.3%. The $\alpha_0^{(b)}$ results are taken as final. We find that two transitions $6s^2\ ^1S_0 - 6s6p\ ^1P_1$ and $6s^2\ ^1S_0 - 6s6p\ ^3P_1$ contribute 99.3% to the valence ground state polarizability for Pb III. Three transitions $6s6p\ ^3P_0 - 6s7s\ ^3S_1$, $6s6p\ ^3P_0 - 6p^2\ ^3P_1$, and

$6s6p\ ^3P_0 - 6s6d\ ^3D_1$ contribute 94.8% to the valence $6s6p\ ^3P_0$ polarizability. Sum of the individual contributions is listed in rows labelled “Sum”. The contribution of the other terms listed in the row “Other” is obtained by subtracting the sum of the contributions that are calculated separately from the total valence polarizability result obtained by the direct solution of the Eq. (1).

Since the $6s^2\ ^1S_0 - 6s6p\ ^1P_1$ transition contributes 90 % to the valence ground state polarizability for Pb III, the $\alpha_0(^1S_0)$ can be estimated using the lifetime of the $6s6p\ ^1P_1$ level. Reshetnikov *et al.* [29] suggested that the measurements of the lifetime of the $ns^2\ ^1S_0 - nsnp\ ^1P_1$ lowest resonance transition can be used to specify the polarizabilities and, alternatively, measurements of the polarizabilities can be used to deduce lifetimes. Moreover, isoelectronic regularities in line strengths can be used to obtain a comprehensive database from a small number of precision lifetime determinations. These methods were applied homologously to produce values for polarizabilities and lifetimes for the Mg, Zn, Cd and Hg isoelectronic sequences [29]. The dipole polarizability α_0 of Pb III given in Ref. [29] was equal to 7.8(6) in a_0^3 units. This number is drastically different from experimental value $\alpha_0 = 13.62(8)\ a_0^3$ given by Hanni *et al.* [16]. The main difference is caused by omission of the core contribution in Ref. [29], which is large and can not be neglected. Our ionic core RPA value (ground state polarizability of Pb^{4+}), 3.63 a.u., is in excellent agreement with the recent measurement, 3.61(4)a.u. [16]. Our final ground state value $\alpha_0 = 13.30\ a_0^3$ is in good agreement with the experimental result $\alpha_0 = 13.62(8)\ a_0^3$ by Hanni *et al.* [16]. Including partial triple excitations into the corrections to the effective Hamiltonian as well as including corrections beyond RPA to the effective dipole operator may further improve accuracy of our approach.

We have estimated the scalar polarizability of the $6s6p\ ^3P_1$ level by the sum-over-state approach, since the direct solution of the Eq. (1) failed to converge for this state. The experimental energies are used in evaluating sum-over-state terms. We have included a large number of levels into the sum-over-state calculation to minimize the error. We estimate that the contribution of the omitted states is on the order of “Other” contributions for the $6s6p\ ^3P_0$ level, which is 1.7%. Therefore, we include the estimated “Other” contribution, 0.163 a.u. The breakdown of all terms is given in Table VI.

V. UNCERTAINTY ESTIMATES AND CONCLUSION

The energies are generally the best experimentally known atomic properties of the system and comparison of the theoretical energy levels with experiment yields important data about the theoretical accuracy. We note that few accurate experimental benchmarks exist for transition properties and polarizabilities of the divalent systems. Therefore, comparison of results obtain with

several different methods of increasing accuracy (such as CI, CI+MBPT, and CI+all-order) is also important for establishing accuracy independently of the comparison with experiment.

The CI+all-order approach has been tested on the calculation of energy levels of B^+ , Al^+ , Mg, Ca, Sr, Zn, Sr, Cd, In^+ , Ba, Hg, and Tl^+ in [5, 14, 15]. The CI + all-order method described above treats electronic correlation in systems with several valence electrons in a significantly more complete way than the CI + MBPT approach [46, 47] due to the inclusion of the additional classes of MBPT terms in Σ_1 and addition of all order (rather than second-order) correction in Σ_2 . At least factor of 3 improvement in agreement with experimental values for the 2-electron binding energies and most excited state energies in comparison with the CI + MBPT method was found.

We also observed significant improvement in the precision of the energy levels with CI+all-order method in comparison with the CI+MBPT one for Pb III. For example, CI+MBPT values for the two-electron binding energy is $607140\ \text{cm}^{-1}$ different from experiment by 1.4%, while our all-order value differs from experiment by only 0.3% (see line one of Table I). We note that we use Pb III ionization energy, $257592(5)\ \text{cm}^{-1}$ from the NIST data [30, 31], the ionization energy of Pb^{3+} , $341435.1(8)\ \text{cm}^{-1}$ was taken from recent experiment [16] to determine experimental two-electron binding energy. Similar (factor of 3-4) improvement is seen for the other energy levels, for example CI+MBPT $6s6p\ ^3P_0$ energy differ from experiment by 5%, while all-order calculation improves agreement to 1.5%. Further improvement in the accuracy of the *ab initio* energy levels may be achieved by the addition of the triple excitations in the all-order calculation.

We note that the agreement of the energy levels with experiment may be significantly improved (to better than 0.1% level) by adjustment of the parameters $\tilde{\epsilon}$ discussed in Section II. The example of such adjustment procedure described in [5]. However, we found that such adjustment may lead to inconsistencies in the polarizability calculation.

We have studied the accuracy of the electric-dipole matrix elements on the example of 7 transitions contributing to the polarizabilities of the $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ states. Since there are no accurate measurements of the corresponding transitions rates, we have conducted four different calculations in order to establish the contributions of the second-order and higher-order corrections to the effective Hamiltonian as well as RPA corrections to the effective dipole operator. These contributions to the electric-dipole matrix elements are summarized in Table VII. The columns 2-4 labeled “CI”, “CI+MBPT”, “CI+all” contain data obtained with the CI, CI+MBPT, CI+all-order methods, respectively. The effective dipole operator D_{eff} includes random phase approximation (RPA) corrections in all these calculations. The column 5 labeled “MBPT contr.” gives the relative difference (in %) between CI and CI+MBPT results.

TABLE VII: Contributions to the electric-dipole matrix elements. The columns 2-4 labeled “CI”, “CI+MBPT”, “CI+all-order” contain data obtained with the CI, CI+MBPT, CI+all-order methods, respectively. The effective dipole operator D_{eff} includes random phase approximation (RPA) corrections in all these calculations. The column 5 labeled “MBPT contr.” gives the relative difference (in %) between CI and CI+MBPT results. The column 6 labeled “All-order contr.” gives the relative difference (in %) between CI+MBPT and CI+all-order results. The column 7 labeled “CI+all-order, No RPA” gives CI+all-order results calculated without RPA corrections in the effective dipole operator. The column 8 labeled “RPA contr.” gives the relative difference (in %) between CI+all-order results calculated with and without RPA correction. Absolute values of matrix elements are given.

Transition	CI RPA	CI+MBPT RPA	CI+all RPA	MBPT contr.	All-order contr.	CI+all No RPA	RPA contr.
$6s^2\ ^1S_0 - 6s6p\ ^1P_1$	2.490	2.360	2.384	-5.5%	1.0%	2.887	-21%
$6s6p\ ^3P_0 - 6p^2\ ^3P_1$	2.065	1.629	1.548	-26.8%	-5.0%	1.897	-23%
$6s6p\ ^3P_0 - 6s6d\ ^3D_1$	0.889	1.437	1.516	38.1%	5.5%	1.673	-10%
$6s6p\ ^3P_0 - 6s7s\ ^3S_1$	0.960	0.935	0.963	-2.7%	3.0%	0.996	-3%
$6s^2\ ^1S_0 - 6s6p\ ^3P_1$	0.483	0.702	0.644	31.2%	-8.3%	0.805	-25%
$6s^2\ ^1S_0 - 6s7p\ ^3P_1$	0.088	0.104	0.102	15.4%	-1.9%	0.020	
$6s^2\ ^1S_0 - 6s7p\ ^1P_1$	0.148	0.092	0.099	-60.9%	7.6%	0.287	

The column 6 labeled “All-order contr.” gives the relative difference (in %) between CI+MBPT and CI+all-order results. The column 7 labeled “CI+all-order, No RPA” gives CI+all-order results calculated without RPA corrections in the effective dipole operator. The column 8 labeled “RPA contr.” gives the relative difference (in %) between CI+all-order results calculated with and without RPA correction. We sorted the transitions by the magnitude of the matrix element, starting from the strongest transitions. The MBPT corrections are large for almost all transitions with the exception of the $6s6p\ ^3P_0 - 6s7s\ ^3S_1$ one. The higher-order all-order corrections are 1–8%, generally increasing for weaker transitions. The RPA corrections are particularly large for the last two transitions which are very weak. In these cases, results without RPA corrections differ by more than a factor of two. The corrections beyond RPA, such as structure radiation, are generally expected to be small for strong E1 transitions.

Based on the size of the all-order corrections we expect the accuracy of our dipole matrix elements to be the highest (1-3%) for the strong transitions. Full all-order treatment of the effective dipole operator should improve the precision and give better estimates of the accuracy of the final values. Further experimental measurements of transition rates between low-lying states would be extremely helpful in benchmark testing of the theoretical methodologies.

In order to establish the accuracy of our polarizability, we also perform the CI and CI+MBPT calculations of the valence polarizabilities carried out with the same parameters (configuration space, basis set, number of partial waves, etc.). No core excitations are added in the pure divalent CI approach. In the CI+MBPT method, core excitations are incorporated by constructing an effective Hamiltonian using second-order many-body perturbation theory [46]. Comparison of the CI, CI+MBPT, and CI+all-order values allows us to evaluate the importance of the various correlation corrections, therefore establish-

ing the upper bound on the uncertainty of our calculations. For the ground state $6s^2\ ^1S_0$ polarizability (calculated with RPA corrections), the CI, CI+MBPT, and CI+all calculations give (in a.u.) 10.56, 9.60, and 9.68, respectively. Therefore, the MBPT and higher-order corrections to the wave functions contribute about 10% and 0.8%, respectively. For the excited state $6s6p\ ^3S_0$ polarizability (calculated with RPA corrections), the CI, CI+MBPT, and CI+all calculations give (in a.u.) 10.12, 9.05, and 9.13, respectively; the MBPT and higher-order corrections are 12% and 0.9%. We note that inclusion of the MBPT and all-order correlations into the effective Hamiltonian produces smaller changes in polarizabilities in comparisons with the matrix elements, owing to some cancelations of the higher-order correlations corrections. In the case of the $6s6p\ ^3P_0$ polarizability, corrections to two dominant transitions, $6s6p\ ^3P_0 - 6p^2\ ^3P_1$ and $6s6p\ ^3P_0 - 6s6d\ ^3D_1$, are nearly the same but with an opposite sign (rows 2 and 3 of Table VII). The RPA ionic core polarizability, which contributes 27% to the total of the ground state polarizability is expected to be accurate to better than 5% [41]. It agrees with experiment to 2%. Considering all of the above uncertainty studies, we expect overall accuracy of our values of $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ polarizabilities to be 1-3% and 3-5%, respectively. The estimate of the ground state polarizability uncertainty is consistent with 2.3% agreement with experiment [16].

In conclusion, we have presented a systematic CI + all-order study of excitation energies, reduced matrix elements, oscillator strengths, and transition rates for Pb III ion. Lifetime values are determined for about 40 levels. Electric-dipole ($6s^2 - 6snp$, $n = 6-12$) matrix elements are calculated to obtain the ground and excited state E1 polarizabilities. The ground state polarizability is in good agreement (2.3%) with recent measurement. Our RPA value for the ground state polarizability of Pb^{+4} , 3.63 a.u. agrees with the recent measurement, 3.61(4)a.u. [16]. Our calculation provide atomic properties of Pb III

for various applications and provide a benchmark test of theory and experiment.

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