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Development of the configuration-interaction + all-order method and application to the parity-nonconserving amplitude and other properties of Pb

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We have developed a significantly more flexible variant of the relativistic atomic method of calculation that combines configuration-interaction and coupled-cluster approaches. The new version is no longer restricted to a specific choice of the initial approximation corresponding to the self-consistent field of the atomic core. We have applied this approach to calculation of different properties of atomic lead, including the energy levels, hyperfine structure constants, electric-dipole transition amplitudes, and $E1$ parity nonconserving (PNC) amplitude for the $6p^2\ ^3P_0$-$6p^2\ ^3P_1$ transition. The uncertainty of the $E1$ PNC amplitude was reduced by a factor of two in comparison with the previous most accurate calculation [V. A. Dzuba *et al.*, Europhys. Lett. **7**, 413 (1988)]. Our value for the weak charge $Q_W = -117(5)$ is in agreement with the standard-model prediction.

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I. INTRODUCTION

Accurate calculation of atomic properties of heavy atoms with several valence electrons is a difficult endeavor. A standard approach in atomic calculations is to separate the atomic electrons into two groups, core and valence electrons. Then, various methods exist to treat core-core, core-valence, and valence-valence correlations. In particular, the valence-valence correlations can be treated in the framework of multiconfiguration Hartree-Fock [1,2], relativistic multiconfiguration Dirac-Fock [3–5], or configuration-interaction (CI) [6–8] methods. The core-core and core-valence correlations can be taken into account using many-body perturbation theory (MBPT) or a more accurate coupled-cluster method [9–11].

A hybrid approach that combines CI and a linearized coupled-cluster method (CI + all-order) have been developed recently [12]. This approach allows us to combine the best features of both methods and accurately treat core-core, core-valence, and valence-valence correlations. It was applied to solve a wide variety of problems requiring calculation of atomic properties ranging from a search for new physics beyond the standard model (SM) of electroweak interactions [13] to the development of state-of-the-art atomic clocks [14,15]. Complexity of calculations increases rapidly with increasing number of valence electrons. While the CI + all-order method has been applied successfully to treat heavy atoms with two, three, and four valence electrons [13,14,16,17] a problem with a choice of starting approximation was identified in Ref. [13]. In the original implementation of the CI + all-order method the initial approximation was limited to the self-consistent Dirac-Fock potential of the closed core.

For example, when calculating properties of Tl, which has three valence electrons, we had to start from the potential of the closed [Xe]$4f^{14}5d^{10}$ core with all three valence electrons removed. Such starting potential is usually referred to as V^{N-3}, where N is the total number of electrons and $(N-3)$ is the number of electrons included in the initial Hartree-Fock-Dirac (HFD) self-consistency procedure. However, that approach led to a problem when calculating electron electric-dipole moment (EDM) enhancement factor and other properties of Tl, in particular, hyperfine structure (HFS) constants. We found that a number of usually small corrections to the matrix elements, such as normalization correction, was unexpectedly large (several percent) in the V^{N-3} approximation, leading to reduced accuracy of the final values.

An alternative approach to accurate Tl calculation is to use better starting approximation for the construction of the basis-set orbitals, i.e., V^{N-1} potential of [Xe]$4f^{14}5d^{10}6s^2$, but then carry out the CI for a three-electron system since *any* orthonormalized single-electron functions can be used as the basis-set orbitals for the CI method. This approach treats Tl as the trivalent system and allows us to account for explicitly such configurations as $6s6p^2$. The complication of this method is an appearance of an extra set of so-called subtraction terms in all-order equations which were previously absent in the all-order approach used in [12].

The goal of this work is to remedy this problem. We derived the linearized coupled-cluster (all-order) equations in arbitrary closed-shell potential and added all of the subtraction terms to the CI + all-order method and corresponding code. We note that flexibility in the choice of the initial potential is also needed for future application of the all-order method to systems with more than four valence electrons, since the quality of the initial V^{N-M} potential, where M is the number of valence electrons, degrades with the increase of M.

We applied the new version of the CI + all-order method to the calculation of the parity-nonconserving (PNC) $6p^2\ ^3P_0$-$6p^2\ ^3P_1$ transition amplitude in Pb. We selected Pb since it is a heavy atom with four valence electrons which can be treated starting from two different potentials, allowing an excellent test of new methodology. Moreover, accurate calculation of the PNC amplitude in Pb is an unsolved problem, with theoretical accuracy still lagging significantly behind the experimental precision.

Atomic parity-violation studies test the SM of the elementary particles in the low-energy sector [18]. All these studies require theoretical calculation of the PNC amplitude for the analysis of the experiments in terms of possible physics beyond the SM. As a result, lack of precision theory for more complicated systems hinders the progress in this field.

Most precise calculation of PNC amplitude was carried out for the $6s$-$7s$ transition in monovalent atomic Cs, with the theoretical uncertainty reaching a few tenths of a percent [19–21]. The uncertainty of the PNC amplitude in the $(6s^26p)\ ^2P^o_{1/2}$-$(6s^26p)\ ^2P^o_{3/2}$ transition of three-valence Tl is an order of magnitude larger [22–24].

The ground-state electronic configuration of Pb atom is $[\mathrm{Xe}]4f^{14}5d^{10}6s^26p^2$. Measurements of PNC optical rotation near the 1.279-μm, $6p^2\ ^3P_0 \rightarrow 6p^2\ ^3P_1$ magnetic dipole transition in Pb were carried out almost 20 yr ago by the Seattle [25,26] and Oxford [27] groups, giving the ratio, R, of the $E1$ PNC to the $M1$ transition amplitude to be $(-9.86 \pm 0.12) \times 10^{-8}$ and $(-9.80 \pm 0.33) \times 10^{-8}$, correspondingly. Thus, the Seattle group achieved the experimental precision of 1.2%.

The quantity R is proportional to Q_W, where the nuclear weak charge Q_W at tree level is given by the formula

$$Q_W \approx -\mathcal{N} + Z\,(1 - 4\sin^2\theta_W), \qquad (1)$$

where $\mathcal{N}$ is the number of neutrons, Z is the nuclear charge, and θ_W is the Weinberg angle. For ^{208}Pb, this expression gives $Q_W \approx -120$. A more accurate SM value, which includes radiative corrections, is $Q_W^{\mathrm{SM}} = -118.79(5)$ [28].

Atomic parity violation tests of the SM are carried out by comparing the SM value of the weak charge with Q_W extracted from the experiment. Such extraction requires an accurate calculation of the quantity R. Due to complicated electronic structure of Pb, there were only a few calculations of the PNC amplitude in the $6p^2\ ^3P_0 \rightarrow 6p^2\ ^3P_1$ transition [29–31]. The most accurate result for R was obtained in [31], where this quantity was determined with 8% uncertainty.

The method development carried out in this work allows us to improve the precision of the PNC amplitude in Pb. Our original implementation of the method required to treat Pb as a system with two valence electrons and construct basis orbitals in the $[\mathrm{Xe}]4f^{14}5d^{10}6s^2\ V^{N-2}$ potential. Another possibility was to consider Pb as a four-valence-electron system and use the $[\mathrm{Xe}]4f^{14}5d^{10}\ V^{N-4}$ potential for the initial self-consistency procedure.

In the present work we extend the CI + all-order method to the case when initial approximation does not correspond to the self-consistent field of the core. A variant of the method allowed us to consider Pb as a system with four valence electrons but use the V^{N-2} potential for the construction of the basis-set orbitals. This potential is expected to provide better initial approximation when combined with full four-valence-electron CI. We report calculations of Pb properties with two choices of the starting potential and conclude that the new method is more reliable and accurate. We calculated the quantity R to be $R = 10.6(4) \times 10^{-8}\, i(-Q_W/\mathcal{N})$, reducing its uncertainty by a factor of 2 in comparison with that seen in [31].

The paper is organized as follows. In Sec. II we describe main features of our method and discuss a choice of initial approximation. In Sec. III we show how the equations, describing core-valence correlations, are modified for a more flexible choice of the potential. In Secs. IV and V we discuss and compare the results obtained in V^{N-2} and V^{N-4} approximations. The last section contains concluding remarks and acknowledgements. If not stated otherwise, atomic units ($\hbar = |e| = m_e = 1$) are used throughout.

II. A CHOICE OF INITIAL APPROXIMATION

Using second quantization, the relativistic no-pair Hamiltonian H can be written as $H = H_0 + V$ [32,33]:

$$H_0 = \sum_i \varepsilon_i \{a_i^\dagger a_i\}, \qquad (2)$$

$$V = \frac{1}{2}\sum_{ijkl} g_{ijkl}\{a_i^\dagger a_j^\dagger a_l a_k\} + \sum_{ij}(V_{\mathrm{DF}} - U_{\mathrm{DF}})_{ij}\{a_i^\dagger a_j\}. \qquad (3)$$

Here $a_i^\dagger$ and a_i are the creation and annihilation operators, respectively; $\{\cdots\}$ designates normal form of operators in respect to the core state Ψ_c: $\{\cdots\}|\Psi_c\rangle = 0$, and the indexes i, j, k, and l range over *all* possible single-electron states. $H_0 = T + U_{\mathrm{DF}}$ is the HFD operator for N_{DF} electrons, forming closed subshells. In this work we do not consider a more general case, when H_0 is not a HFD operator.

Two-particle matrix elements (MEs), designated as g_{ijkl}, are given by

$$g_{ijkl} = \int dr^3 dr'^3 \psi_i^\dagger(\mathbf{r})\psi_j^\dagger(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{r})\psi_l(\mathbf{r}'),$$

where ψ_i are the single-electron wave functions and V_{DF} is the frozen-core Dirac-Fock (DF) potential determined as

$$(V_{\mathrm{DF}})_{ij} = \sum_{b=1}^{N_c}(g_{ibjb} - g_{ibbj}) \equiv \sum_{b=1}^{N_c}\tilde{g}_{ibjb}, \qquad (4)$$

with N_c being the number of the core electrons.

There is certain flexibility in choosing potential U_{DF}, which defines initial approximation H_0 and enters Eq. (3). It is convenient to determine U_{DF} as the DF potential for N_{DF} electrons:

$$(U_{\mathrm{DF}})_{ij} \equiv \sum_{b=1}^{N_{\mathrm{DF}}}\tilde{g}_{ibjb}. \qquad (5)$$

For monovalent atoms the natural choice is $N_{\mathrm{DF}} = N_c = N - 1$, which leads to $U_{\mathrm{DF}} = V_{\mathrm{DF}}$. This is often referred to as V^{N-1} approximation. With such a choice the second term in Eq. (3) vanishes.

For multivalent atoms it is sometimes convenient to choose $N_{\mathrm{DF}} > N_c$. The dominant configuration of Pb ground state is $[\cdots]\,6s^26p^2$; thus, Pb can be considered as an atom with four valence electrons. However, we can include two $6s$ electrons, forming a closed subshell, in the initial HFD self-consistency procedure and construct the basis set in the V^{N-2} approximation. Then the number of the core electrons is $N_c = N - 4$, while $N_{\mathrm{DF}} = N - 2 > N_c$. As a result, there will be only a partial cancellation of the terms determined by the potential V_{DF} and the DF field U_{DF} in Eq. (3).

We designate the difference between V_{DF} and U_{DF} as U. Then, for a single-electron ME:

$$U_{ij} = (U_{\mathrm{DF}} - V_{\mathrm{DF}})_{ij}. \tag{6}$$

Angular reduction for this potential and the Coulomb MEs is given in Appendix A.

III. EFFECTIVE HAMILTONIAN FOR MULTIVALENT ATOMS

The wave functions and energy levels of the valence electrons can be found by solving the multiparticle relativistic equation [34],

$$H_{\mathrm{eff}}(E_n)\Phi_n = E_n\Phi_n, \tag{7}$$

where the effective Hamiltonian is defined as

$$H_{\mathrm{eff}}(E) = H_{\mathrm{FC}} + \Sigma(E), \tag{8}$$

with H_{FC} being the Hamiltonian in the frozen-core approximation. The energy-dependent operator $\Sigma(E)$ accounts for virtual excitations of the core electrons. It is constructed using the second-order MBPT in the CI + MBPT approach [34] or linearized coupled cluster single-double (LCCSD) method in the CI + all-order approach [12].

It is convenient to decompose the effective Hamiltonian $H_{\mathrm{eff}}(E)$ into two parts $H_{\mathrm{eff}}(E) = H_1 + H_2$, where H_1 represents the one-body part of the Hamiltonian and H_2 represents the two-body part of the Coulomb interaction. In this work, we disregard the Breit interaction as well as three-electron part of the effective Hamiltonian [34].

The energy-dependent operator Σ is also separated into two parts, $\Sigma = \Sigma_1 + \Sigma_2$, where Σ_1 and Σ_2 describe one- and two-body parts of core-valence correlations, respectively. The expressions for single-electron MEs of these operators, $(\Sigma_1)_{ij}$ and $(\Sigma_2)_{ijkl}$, obtained in the LCCSD method approximation for the case $U = 0$ (i.e., when $U_{\mathrm{DF}} = V_{\mathrm{DF}}$), are given and discussed in detail in Ref. [12].

In the case of $U \neq 0$, we should add the terms linear in U to the equations for the cluster amplitudes calculated in the framework of the LCCSD approximation. The resulting LCCSD equations derived for this more general case are presented below:

$$\Sigma_{ma} = \mathrm{LCCSD}\ - U_{ma} + \sum_b \rho_{mb} U_{ba} - \sum_n \rho_{na} U_{mn} - \sum_{bn} \tilde{\rho}_{mnab} U_{bn}, \tag{9a}$$

$$\Sigma_{mnab} = \mathrm{LCCSD}\ - \sum_r \tilde{\rho}_{mrab} U_{nr} + \sum_c \tilde{\rho}_{mnac} U_{cb}, \tag{9b}$$

$$\Sigma_{mv} = \mathrm{LCCSD}\ + \sum_b \frac{\Sigma_{mb} U_{bv}}{\tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_b - \varepsilon_m} - \sum_{bn} \frac{\tilde{\Sigma}_{mnvb} U_{bn}}{\tilde{\varepsilon}_v + \varepsilon_b - \varepsilon_{mn}}, \tag{9c}$$

$$\Sigma_{mnva} = \mathrm{LCCSD}\ - \sum_r \frac{\tilde{\Sigma}_{mrva} U_{nr}}{\tilde{\varepsilon}_v + \varepsilon_a - \varepsilon_{mr}} + \sum_c \frac{\Sigma_{mnvc} U_{ca}}{\tilde{\varepsilon}_v + \varepsilon_c - \varepsilon_{mn}} + \sum_c \frac{\Sigma_{nmac} U_{cv}}{\tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_{ca} - \varepsilon_{mn}}, \tag{9d}$$

$$\Sigma_{mnvw} = \mathrm{LCCSD}\ + \sum_c \left(\frac{\Sigma_{mnvc} U_{cw}}{\tilde{\varepsilon}_v + \tilde{\varepsilon}_w - \varepsilon_w + \varepsilon_c - \varepsilon_{mn}} + \frac{\Sigma_{nmwc} U_{cv}}{\tilde{\varepsilon}_w + \tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_c - \varepsilon_{mn}} \right), \tag{9e}$$

where $\Sigma_{ij} \equiv (\Sigma_1)_{ij}$, $\Sigma_{ijkl} \equiv (\Sigma_2)_{ijkl}$, and ε_i are one-electron DF energies and we use notation $\varepsilon_{ij} \equiv \varepsilon_i + \varepsilon_j$. The symbol tilde over $\varepsilon_{v,w}$ reflects the fact that the effective Hamiltonian (8) is energy dependent [12]. A definition of the tided energy depends on the choice of initial approximation and is discussed in Sec. IV.

The terms labeled "LCCSD" in Σ_{mv}, Σ_{mnva}, and Σ_{mnvw} are given by the right-hand sides of Eqs. (22)–(24) in Ref. [12]. The core amplitudes Σ_{ma} and Σ_{mnab} are obtained from the core coefficients ρ_{ma} and ρ_{mnab} (given, for example, in [35]) using simple relations

$$\begin{aligned} \Sigma_{ma} &= \rho_{ma}(\varepsilon_a - \varepsilon_m), \\ \Sigma_{mnab} &= \rho_{mnab}(\varepsilon_a + \varepsilon_b - \varepsilon_m - \varepsilon_n). \end{aligned} \tag{10}$$

It is easy to verify that the expressions for Σ_{mnva} and Σ_{mnvw} remain the same when we transpose the indexes $m \leftrightarrow n$ and $a \leftrightarrow v$ (or $m \leftrightarrow n$ and $w \leftrightarrow v$), maintaining original symmetry of the all-order LCCSD equations. We performed angular reduction and obtained the formulas given in the Appendix B.

IV. V^{N-2} APPROXIMATION

In this section we describe a construction of the basis set and calculation of the low-lying energy levels, HFS constants, $E1$ transition amplitudes, and $E1$ PNC amplitude for the $6p^2\ {}^3P_0$-$6p^2\ {}^3P_1$ transition in V^{N-2} approximation.

A. Basis set and energy levels

The basis set was constructed in the framework of Dirac-Fock-Sturm (DFS) approach. We start from a solution of the DF equations (disregarding the Breit interaction) for the $[1s^2,\ldots,5d^{10},6s^2]$ closed shells,

$$\hat{H}_0\,\psi_c = \varepsilon_c\,\psi_c, \tag{11}$$

where H_0 is the relativistic DF Hamiltonian [12,34] and ψ_c and ε_c are the single-electron wave functions and energies, respectively. Note that both $6s$ electrons were included in the initial self-consistency procedure.

As a next step, all orbitals up to the $6s$ were frozen and the $7,8s$, 6–$8p$, $6d$, and $4f$ orbitals were constructed in respective V^{N-2} potential. Higher virtual orbitals were obtained by solving the DFS equations described in [36,37]. The resulting basis set includes the DF functions for the occupied core and valence orbitals and the DFS functions for virtual orbitals and contains six partial waves with the orbitals up to $32s$, $32p$, $32d$, $30f$, $25g$, and $25h$.

At the stage of CI calculation we consider Pb as a four-valence atom. We construct the set of configurations that contains single and double excitations of the electrons

TABLE I. V^{N-2} approximation. Theoretical and experimental [38] energy levels of Pb (in cm^{-1}). Four-electron binding energies are given in the first row for the ground state; energies in other rows are counted from the ground state. Experimental binding energy of the ground state is calculated as a sum of four ionization potentials (IPs): IP(Pb$^+$) + IP(Pb^{2+}) + IP(Pb^{3+}) + IP(Pb^{4+}). Results of the CI, CI + MBPT, and CI + all-order calculations are given in columns labeled "CI", "CI + MBPT", and "CI + all". Corresponding relative differences of these three calculations with the experiment are given in percentages. In the second column the electronic terms from the National Institute of Standards and Technology (NIST) database [38] are listed. In the third column the electronic terms obtained in this calculation are given, when they differ from the NIST's ones. In columns 4–6 we give the Landé g factors for the present calculation, LS-coupling scheme, and the experiment.

	Term		g factor							Differences (%)		
Configuration	NIST	Present	(calc.)	LS coupling	(exp.)	CI	CI + MBPT	CI + all	Experiment	CI	CI + MBPT	CI + all
$6p^2$	$^3P_0$					756 855	780 823	782 396	780 092	3.0	−0.1	−0.3
$6p^2$	$^3P_1$		1.499	1.500	1.501	7093	7697	7710	7819	9.3	1.6	1.4
$6p^2$	$^3P_2$		1.277	1.500	1.269	9913	10 585	10587	10650	6.9	0.6	0.6
$6p^2$	$^1D_2$		1.223	1.000	1.230	19 965	21 401	21440	21458	7.0	0.3	0.1
$6p^2$	$^1S_0$					28 084	29 707	29 808	29467	4.7	−0.8	−1.2
$6p7p$	$^3P_1$	$^3D_1$	0.671	0.500		40 732	42 528	42 755	42 919	5.1	0.9	0.4
$6p7p$	$^3P_0$					42 303	44 059	44 299	44 401	4.7	0.8	0.2
$6p7p$	$^3D_1$	$^3P_1$	1.469	1.500		42 486	44 299	44 522	44 675	4.9	0.8	0.3
$6p7p$	$^3D_2$		1.173	1.167		42 630	44 438	44 657	44 809	4.9	0.8	0.3
$6p7s$	$^3P^o_0$					33 104	34 634	34 917	34 960	5.3	0.9	0.1
$6p7s$	$^3P^o_1$		1.350	1.500	1.349	33 451	34 959	35 243	35 287	5.2	0.9	0.1
$6p6d$	$^3F^o_2$		0.790	0.667	0.796	43 818	45 660	45 933	45 443	3.6	−0.5	−1.1
$6p6d$	$^3D^o_2$		1.254	1.167	1.247	44 631	46 458	46 756	46 061	3.1	−0.9	−1.5
$6p6d$	$^3D^o_1$		0.883	0.500	0.864	44 714	46 515	46 820	46 068	2.9	−1.0	−1.6
$6p6d$	$^3F^o_3$		1.122	1.083	1.116	45 187	46 824	47 134	46 329	2.5	−1.1	−1.7
$6p7s$	$^3P^o_2$		1.486	1.500	1.496	45 629	47 959	48 282	481 89	5.3	0.5	−0.2

from lowest-lying configurations ($6s^2\,6p^2$, $6s^2\,6p\,7p$, and $6s^2\,6p\,8p$ for even-parity states and $6s^2\,6p\,7s$, $6s^2\,6p\,6d$, and $6s^2\,6p\,8s$ for odd-parity states) to the 7–22s, 6–22p, 6–17d, 4–16f, and 5–8g orbitals. We checked that triple excitations from the low-lying configurations only slightly change the energy levels. Then we solved the multiparticle relativistic Schrödinger equation for four valence electrons to find the eigenvectors and eigenvalues for the low-lying states.

To illustrate the role of core-valence correlations we calculated the low-lying energy levels using three different approaches of increasing accuracy: (i) the conventional CI method, (ii) the framework of the approach combining CI with the second order of MBPT (CI + MBPT method [34]), and (iii) the CI method combined with LCCSD method (CI + all-order approach [12]) modified as discussed in Sec. III.

Calculations at the CI + MBPT and CI + all-order stages require knowledge of MEs of the operator Σ. We emphasize that for the V^{N-2} approximation $N_{\rm DF} > N_c$ and $U \neq 0$ and the modified equations (B1) should be used. These equations include tilded one-electron energies $\tilde{\varepsilon}_v$ of valence orbitals, which still have to be defined. When we are interested only in the low-lying energy levels, an energy dependence of the effective Hamiltonian (8) can be usually neglected for the properly chosen $\tilde{\varepsilon}_v$. The recipe of Ref. [12] is to put $\tilde{\varepsilon}_v = \varepsilon_{v_0}$, where v_0 is the lowest valence orbital for the particular partial wave. Here we found that the best choice is

$$\tilde{\varepsilon}_v = \varepsilon_{v_0} - U_{v_0v_0}, \tag{12}$$

where $U_{v_0v_0}$ can be obtained from Eq. (5). Effectively, this means that we choose $\tilde{\varepsilon}_v$ to be the DF energy of the lowest valence orbital for the given partial wave in the V^{N-4} potential.

The results of the energy-level calculations are presented in Table I. We find that the accuracy of the CI + MBPT energies was improved by a factor of 2.5 to 30 in comparison with the CI results for all energy levels. We note that a number of energy levels were reproduced with an accuracy of a few tenths of a percent at the CI + MBPT stage. For such a heavy multivalent atom as Pb, it looks unexpectedly good and is probably accidental. For this reason further improvement of an agreement between the theoretical and the experimental energy levels at the CI + all-order stage is difficult. Both methods underestimate transition energies to the levels of the $6p\,6d$ configuration, but the results obtained at the CI + MBPT stage are slightly closer to the experimental values. For almost all other energy levels the CI + all-order approach gives better agreement with the experiment, with the average difference with experiment being 0.6%.

Our calculation of g factors for the low-lying states revealed a discrepancy with the NIST database [38] for two electronic terms. In the second column we present the electronic terms provided by NIST [38]. In the third column we give our assignment when it differs from the NIST terms. In columns 4–6 we present g factors obtained in our calculation, the values corresponding to the LS-coupling scheme, and the experimental numbers. We see rather good agreement between theory and experiment for all cases where experimental g factors are known. For the $6p7p$ configuration, the experimental g factors are unknown. Calculated g factors indicate some mixing between LS terms and support new assignments. We note that for the less-than-half-filled p shell one should expect "normal" order of levels of the ^3P_J triplet, when the levels with smaller J are lying lower (see, e.g., the book of Sobelman [39]). Our term assignments are in agreement with this rule.

TABLE II. V^{N-2} approximation. The breakdown of different contributions to the magnetic dipole HFS constants A (in MHz). The CI + MBPT and CI + all-order values are presented in the third and fourth columns, correspondingly. The remaining columns give various corrections described in the text. Values labeled "Total" are obtained as $A(\mathrm{CI+all}) + \mathrm{RPA} + \mathrm{Sbt} + \sigma + \mathrm{SR} + \mathrm{Norm}$. The recommended values, labeled as "Recomm.", are obtained as $A(\mathrm{CI+all}) + \mathrm{RPA} + \mathrm{Sbt} + \sigma + (1/2)\mathrm{SR} + \mathrm{Norm}$ (see an explanation in the text). The last three columns are the experimental results available in the literature.

	CI	CI + MBPT	CI + all	RPA	Sbt	σ	SR	Norm	Total	Recomm.	Refs. [41,42]	Ref. [43]	Ref. [40]
$6p^2\ {}^3P_1$	−2184	−2545	−2513	46	−28	118	−116	45	−2449	−2392	−2416(36)		−2389.4(0.7)
$6p^2\ {}^3P_2$	2067	2335	2369	341	9	−96	−122	−48	2453	2513	2739(10)		2600.8(0.9)
$6p^2\ {}^1D_2$	481	499	519	139	−2	−7	−121	−11	518	577	620(6)	609.820(8)	
$6p7p\ {}^3P_1$	5914	6635	6649	434	−24	−271	−83	−92	6614	6654			
$6p7p\ {}^3D_1$	−2536	−2886	−2888	−181	11	122	27	39	−2868	−2882			
$6p7p\ {}^3D_2$	2811	3144	3154	227	−9	−128	−47	−44	3153	3176			
$6p7s\ {}^3P_1^o$	7785	8536	8528	632	121	−329	−74	−123	8753	8790	8819(14)		8802.0(1.6)
$6p6d\ {}^3F_2^o$	2633	2989	2998	205	−5	−120	−42	−45	2990	3011	3094(9)		
$6p6d\ {}^3D_2^o$	−827	−1482	−1482	−94	13	65	17	33	−1448	−1456			
$6p6d\ {}^3D_1^o$	−2462	−2808	−2816	−156	−68	120	−10	41	−2889	−2884			
$6p6d\ {}^3F_3^o$	1779	1993	2000	140	81	−82	−27	−44	2066	2079	2072(8)		
$6p7s\ {}^3P_2^o$	1336	1593	1604	287	−40	−43	−94	−26	1688	1734			

B. Hyperfine structure constants

Our goal is to calculate the $E1$ PNC amplitude, which is sensitive to the behavior of the wave functions at the nucleus. To test the quality of the wave functions in the vicinity of the nucleus, we carried out calculation of the magnetic dipole HFS constants A for the even- and odd-parity low-lying states. We calculate the $E1$ PNC amplitude for the zero-spin isotope ^{208}Pb, which was used in the experiments [25,27]. Our results for the HFS constants correspond to the ^{207}Pb isotope that has nuclear spin $I = 1/2$ and the magnetic moment $\mu/\mu_N \approx 0.5783$ [40], where μ_N is the nuclear magneton.

For an accurate calculation of the HFS constants we take into account not only random-phase approximation (RPA) corrections but also the corrections beyond RPA, including one- and two-particle subtraction contributions (their sum is labeled as "Sbt"), the core-Brueckner (σ), structural radiation (SR), and normalization (Norm) corrections [44]. The results of the calculation are presented in Table II.

The values in the column labeled "Total" were found as the sum of the values obtained at the CI + all-order stage plus the corrections listed in Table II, i.e., $A(\mathrm{Total}) = A(\mathrm{CI+all}) + \mathrm{RPA} + \mathrm{Sbt} + \sigma + \mathrm{SR} + \mathrm{Norm}$. We find that the corrections (beyond RPA) are sufficiently large, as demonstrated in Table II. In particular, they are very significant for the even-parity states belonging to the $6p^2$ configuration. For example, the absolute value of the RPA correction is 2.5 times smaller than the SR correction for the $6p^2\ {}^3P_1$ state. We can explain it as follows. The main configuration, contributing 94% in probability to this state, is $6p_{1/2}\,6p_{3/2}$. Single-electron contributions of the $6p_{1/2}$ and $6p_{3/2}$ electrons to the HFS constant $A(6p^2\ {}^3P_1)$, are such that they tend to cancel each other. This holds for the "bare" H_{hfs} operator and when we include the RPA corrections. As a result, the total RPA correction is not large. The SR corrections to the single-electron contributions of the $6p_{1/2}$ and $6p_{3/2}$ electrons, in contrast, are added, resulting in a large contribution to the HFS constant.

It is worth noting that we calculate the SR corrections only in the second order of the MBPT. Usually the second order of the MBPT overestimates the respective contribution. We assume that an inclusion of higher orders (beyond second order) will reduce the absolute value of the SR contribution. Our values in the column labeled "Recomm." were obtained as described above, with the SR corrections reduced by a factor of two; i.e., $A(\mathrm{Recomm.}) = A(\mathrm{CI+all}) + \mathrm{RPA} + \mathrm{Sbt} + \sigma + (1/2)\mathrm{SR} + \mathrm{Norm}$. The difference between calculated and recommended values does not exceed 4% except for the level $6p^2\ {}^1D_2$. The ${}^1D_2$ HFS constant is a few times smaller than the other, but the SR correction is of comparable size, contributing at the level of 20%. It leads to a slightly larger difference (5.4%) between our value and the most accurate experimental result [43].

Our recommended values for the HFS constants show better agreement with the experimental results [40,43]. Note that the experimental values [41,42] are less accurate. Moreover, their value for the $6p^2\ {}^3P_2$ level disagrees both with the experiment [40] and with our calculation. Therefore, we do not rely on this experimental result in estimating the accuracy of our value for the HFS $6p^2\ {}^3P_2$ constant. Using remaining experimental data and considering the difference between the CI + MBPT and CI + all-order results, as well as the size of the SR correction, we estimate the theoretical uncertainties of the HFS constants to be at the level of 4%.

C. $E1$ transition amplitudes and polarizability

The expression for the $E1$ PNC amplitude (in the second order of the perturbation theory) involves also the MEs of the electric-dipole operator. As a result, it is sensitive to the behavior of the wave functions at long distances. To test it we calculated a number of $E1$ transition amplitudes relevant to the $E1$ PNC amplitude of the $6p^2\ {}^3P_0 \rightarrow 6p^2\ {}^3P_1$ transition. We also calculated the value of the $6p^2\ {}^3P_0$ ground-state static polarizability.

For the $E1$ MEs, all corrections beyond RPA (in contrast with the HFS constants) are relatively small and we present only the final values of a few most important MEs. These values are obtained in the same way as above: $D(\mathrm{Total}) = D(\mathrm{CI+all}) + \mathrm{RPA} + \mathrm{Sbt} + \sigma + \mathrm{SR} +$

TABLE III. V^{N-2} approximation. The reduced MEs $|\langle f||d||i\rangle|$ (in a.u.) for the electric-dipole transitions, obtained in the CI+all-order approximation and including RPA, Sbt, σ, SR, and normalization corrections. In last column the MEs extracted from the experimental transition probabilities are presented. The value of the ground-state static polarizability is given in the last line.

Transition	This work	Experiment
$6p^2\ ^3P_1$-$6p7s\ ^3P_0^o$	1.89	2.04(7)[a] 2.05(10)[b]
$6p^2\ ^3P_0$-$6p7s\ ^3P_1^o$	1.32	1.37(4)[a] 1.20(5)[c]
$6p^2\ ^3P_0$-$6p6d\ ^3D_1^o$	2.01	1.62(4)[a] 1.67(8)[b]
$\alpha(6p^2\ ^3P_0)$	46.5	47(7)[d]

[a] Reference [45].
[b] Reference [48].
[c] Reference [46].
[d] Reference [47].

Norm, where $D \equiv |\langle\gamma'||d||\gamma\rangle|$ and $\mathbf{d} = -\mathbf{r}$ is the electric dipole operator.

The calculated MEs are presented in Table III and compared with the values extracted from the experimental transition probabilities. Unfortunately, the accuracy of the available experimental data is not very high. For example, the difference between results of [45] and [46] for the $\langle 6p^2\ ^3P_0||d||6p7s\ ^3P_1^o\rangle$ ME is about 12%. For two transitions our calculated values agree with the experiment, taking into account their error bars. However, for the transition $6p^2\ ^3P_0$-$6p6d\ ^3D_1^o$ our result differs from the experiment by 20%. We do not see an obvious reason for this discrepancy.

To further test the accuracy of the $E1$ transition amplitudes from the ground-state $6p^2\ ^3P_0$, we calculated its static polarizability. Our value, 46.5 a.u., is in a very good agreement with the central value of the experimental result, 47(7) a.u. [47].

D. PNC amplitude

The PNC nuclear spin-independent part of electron-nuclear interaction can be written as

$$H_{\rm PNC} = -\frac{G_F}{2\sqrt{2}}\, Q_W \gamma_5 \rho(\boldsymbol{r}), \tag{13}$$

where $G_F \approx 2.2225 \times 10^{-14}$ a.u. is the Fermi constant of the weak interaction, Q_W is the nuclear weak charge given by Eq. (1), γ_5 is the Dirac matrix, and $\rho(\boldsymbol{r})$ is the nuclear density distribution.

We assume that the nucleus is a uniformly charged ball,

$$\rho(\boldsymbol{r}) = \frac{3}{4\pi R^3}\Theta(R-r),$$

where $\Theta(R-r)$ is the Heaviside step function. The root-mean-square (rms) charge radius for ^{208}Pb was measured to be $R_{\rm rms} = 5.5010$ fm [49]. Using the formula $R = \sqrt{5/3}\, R_{\rm rms}$, we find $R \approx 7.1108$ fm.

If $|i\rangle$ and $|f\rangle$ are the initial and final atomic states of the same nominal parity then, to the lowest nonvanishing order, the electric-dipole transition ME is equal to

$$\langle f|d_{q,\rm PNC}|i\rangle = \sum_n \left[\frac{\langle f|d_q|n\rangle\langle n|H_{\rm PNC}|i\rangle}{E_i - E_n} + \frac{\langle f|H_{\rm PNC}|n\rangle\langle n|d_q|i\rangle}{E_f - E_n}\right], \tag{14}$$

where E_i, E_f, and E_n are the energies of the initial, final, and intermediate states, respectively, $q = 0,\pm 1$, and $|a\rangle \equiv |J_a, M_a\rangle$, with J_a and M_a being the total angular momentum and its projection.

Taking into account that $H_{\rm PNC}$ is a pseudoscalar operator, i.e., its ME is nonzero only for the states with the same J and M, we can determine the spin-independent PNC amplitude of the $6p^2\ ^3P_0 \to 6p^2\ ^3P_1$ transition, $E1_{\rm PNC}$, as the reduced ME of the operator $d_{q,\rm PNC}$:

$$\begin{aligned} E1_{\rm PNC} \equiv \langle f||d_{\rm PNC}||i\rangle &= \sum_n \left(\frac{\langle ^3P_1||d||n\rangle\langle n|H_{\rm PNC}|^3P_0\rangle}{E_{^3P_0} - E_n} + \frac{\langle ^3P_1|H_{\rm PNC}|n\rangle\langle n||d||^3P_0\rangle}{E_{^3P_1} - E_n}\right) \\ &\equiv E1^{(1)}_{\rm PNC} + E1^{(2)}_{\rm PNC}. \end{aligned} \tag{15}$$

Introducing notations

$$|\delta\psi_1\rangle = \sum_n \frac{|n\rangle\langle n|H_{\rm PNC}|^3P_0\rangle}{E_{^3P_0} - E_n}, \tag{16a}$$

$$\langle\delta\psi_2| = \sum_n \frac{\langle ^3P_1|H_{\rm PNC}|n\rangle\langle n|}{E_{^3P_1} - E_n}, \tag{16b}$$

we express $E1^{(1)}_{\rm PNC}$ and $E1^{(2)}_{\rm PNC}$ as

$$E1^{(1)}_{\rm PNC} = \langle ^3P_1||d||\delta\psi_1\rangle, \tag{17a}$$

$$E1^{(2)}_{\rm PNC} = \langle\delta\psi_2||d||^3P_0\rangle. \tag{17b}$$

The $E1_{\rm PNC}$ amplitude is sensitive to the MEs of the weak interaction $H_{\rm PNC}$, $E1$ transition amplitudes, and the energy spectrum. The weak interaction depends on the wave function in the vicinity of the nucleus and, in this respect, is similar to the MEs of the hyperfine interaction. Thus, we are able to estimate the accuracy of the calculation of the PNC amplitude analyzing the accuracy of the HFS constants and $E1$ transition amplitudes.

In calculating the PNC amplitude we included the RPA corrections, one- and two-particle subtraction contributions, the core-Brueckner, SR, and normalization corrections, as we did when calculated the HFS constants.

When the $E1_{\rm PNC}$ transition amplitude is obtained, we are able to find the quantity

$$\mathcal{R} = \frac{{\rm Im}(E1_{\rm PNC})}{M1}, \tag{18}$$

where we take into account that $E1_{\rm PNC}$ is imaginary and designate the reduced ME of the magnetic dipole operator μ: $M1 \equiv \langle 6p^2\ ^3P_1||\mu||6p^2\ ^3P_0\rangle$. The quantity $\mathcal{R}$ was experimentally determined in [25–27], so we are able to compare theory and experiment.

TABLE IV. V^{N-2} approximation. The breakdown of different contributions to the terms $E1^{(1)}_{\rm PNC}$ and $E1^{(2)}_{\rm PNC}$ determined by Eq. (15) (in a.u.). The values of $M1 \equiv \langle 6p^2\ ^3P_1\,||\mu||6p^2\ ^3P_0\rangle$ are in the Bohr magnetons. The values of R are given in units $10^{-8}(-Q_W/N)$. The first, second, and third lines give the CI, CI + MBPT, and CI + all-order values, respectively. The following lines give various corrections described in the text. Numbers labeled "Total" are obtained as (CI + all) + RPA + σ + SR + Sbt + Norm. Numbers labeled "Recomm." are obtained as (CI + all) + RPA + σ + (1/2)SR + Sbt + Norm (see the explanation in the text).

	$E1^{(1)}_{\rm PNC}$	$E1^{(2)}_{\rm PNC}$	$M1$	R
CI	2.619	2.109	−1.297	−9.99
CI + MBPT	2.768	2.495	−1.292	−11.16
CI + all	2.718	2.488	−1.293	−11.03
RPA	0.344	−0.312		−0.07
σ	−0.099	−0.077		0.37
SR	−0.032	0.086		−0.11
Sbt	−0.007	0.021		−0.03
Norm	−0.055	−0.042		0.21
Total	2.869	2.164	1.293	−10.66
Recomm.	2.885	2.121	1.293	−10.6(4)
Other				−10.4(8)[a]
				−11.4[b]
				−13[c]

[a] Reference [31].
[b] Reference [30].
[c] Reference [29].

The results of calculation of both $E1^{(1)}_{\rm PNC}$ and $E1^{(2)}_{\rm PNC}$ terms, determined by Eq. (15), are presented in Table IV. Our analysis shows that the intermediate state $6p7s\ ^3P^o_0$ gives a dominating (∼86%) contribution to $E1^{(1)}_{\rm PNC}$. Thus, the contribution of higher-lying states is rather small.

For the $E1^{(2)}_{\rm PNC}$ part of the $E1_{\rm PNC}$ amplitude the situation is quite different. Two lowest-lying odd-parity states with $J = 1$ listed in Table I contribute to $E1^{(2)}_{\rm PNC}$ with different signs and their total contribution is negative; i.e., it has a different sign in comparison with the total value of $E1^{(2)}_{\rm PNC}$. As a result, higher-lying states give a very large contribution to this amplitude.

Such anomalously large contribution comes from the high-lying odd-parity states belonging to the configuration $6s\,6p^3$. According to our calculation the lowest state with $J = 1$, belonging to this configuration, is lying ∼74 000 cm^{-1} above the ground state. The MEs of the electric-dipole and $H_{\rm PNC}$ operators are large: $\langle 6s^26p^2\ ^3P_0\,||D||6s6p^3\ J = 1\rangle = 1.91$ a.u. and $\langle 6s6p^3\ J = 1|H_{\rm PNC}|6s^26p^2\ ^3P_1\rangle = 476$ a.u.. As a result, the contribution of this odd-parity state to $E1^{(2)}_{\rm PNC}$ is large and positive.

It is worth noting that, for the reason discussed above, a direct summation over intermediate states is not applicable for the calculation of $E1^{(2)}_{\rm PNC}$. Instead, we solve an inhomogeneous equation [50] which accounts for contribution from all discrete states and a continuum.

Analyzing the RPA and other corrections to $E1^{(1)}_{\rm PNC}$ and $E1^{(2)}_{\rm PNC}$, we see that large RPA corrections have different signs for these two amplitudes. Accidentally, these contributions turned out to be close in their absolute values and essentially cancel each other in the sum $E1^{(1)}_{\rm PNC} + E1^{(2)}_{\rm PNC}$. For this reason the role of smaller corrections (σ, Sbt, etc.) is enhanced.

A procedure of including the RPA, σ, and SR corrections in calculating $E1_{\rm PNC}$ is reduced to "dressing" the $H_{\rm PNC}$ and **d** operators, as described in detail in [44]. To find the subtraction and normalization corrections, following the recipe of Ref. [44], we obtained $|\delta\psi_1\rangle$ and $|\delta\psi_2\rangle$, given by Eq. (16), for the effective operator $H^{\rm eff}_{\rm PNC}$ and then calculated the MEs in (17) for the effective electric-dipole operator $\mathbf{d}^{\rm eff}$.

The values listed in the row labeled "Total" of Table IV were obtained as the sum of the CI + all values plus different corrections including RPA, σ, SR, Sbt, and Norm. As we discussed above, the SR corrections turn out to be overestimated in the second order of the MBPT. We had reduced these corrections by a factor of 2 to obtain the recommended values of the HFS constants. We assume that the same procedure should be used for the PNC amplitude as well, though in this case the SR corrections are not so significant as for the HFS constants. The results listed in the row labeled "Recomm." are obtained as the "Total" values but we add only a half of the SR correction. According to our estimate, the excitations of the core electrons contribute to $E1_{\rm PNC}$ less than 0.1% and we neglect this contribution.

The RPA and other similar corrections are very small for the $M1$ ME $\langle 6p^2\ ^3P_1\,||\mu||6p^2\ ^3P_0\rangle$ and can be neglected without loss of accuracy. We present the values of the quantity R [given by Eq. (18)] obtained in different approximations in the last column of the table. Various corrections to R are listed as well. Our recommended value is $R = -10.6(4) \times 10^{-8}\,(-Q_W/\mathcal{N})$. Based on the calculation accuracy of the HFS constants, $E1$ transition amplitudes, and the ground state polarizability, we assign to the quantity R the uncertainty ∼4%. Our result is in a good agreement with earlier calculations [29–31] but the accuracy is two times higher.

Using our recommended value of R and the most accurate experimental value $(-9.86 \pm 0.12) \times 10^{-8}$ [25,26], we find the weak nuclear charge for ^{208}Pb to be $Q_W = -117(5)$. This value is in good agreement with the SM prediction $Q^{\rm SM}_W = -118.79(5)$ [28]. Note that our theoretical error (4%) is more than three times larger than the experimental error (1.2%). Therefore, we need further improvement of the theory for more accurate calculations. A next step in improving accuracy would be to treat SR corrections to all orders.

V. V^{N-4} APPROXIMATION

It is worth noting that, due to importance of the $6s6p^3$ configuration for the $E1_{\rm PNC}$ amplitude discussed above, a two-electron calculation of Pb using the V^{N-2} approximation gives poor results. In this section, as earlier, we consider Pb as the four-valence-atom using V^{N-4} approximation and compare results with those obtained previously in the V^{N-2} approximation. Both calculations are similar, so we focus here only on the points where these two approaches differ from each other.

The basis set was constructed using the DFS approach, but the DF equations were solved for the $[1s^2,\ldots,5d^{10}]$ closed core; i.e., the $6s$ electrons were excluded from the self-consistency procedure. Next, the 6–8s, 6–8p, $6d$, and $4f$ orbitals were constructed in the field of the frozen-

TABLE V. The energy levels (in cm^{-1}) obtained using the CI + all-order method in V^{N-2} and V^{N-4} approximations are compared with the experiment [38]. Four-electron binding energies are given in the first row for the ground state; energies in other rows are counted from the ground state. Corresponding relative differences of these two calculations with the experiment are given in percentages. Electronic terms in the second column correspond to the new assignment discussed in text.

		CI + all			Diff. (%)	
Configuration	Term	V^{N-4}	V^{N-2}	Experiment	V^{N-4}	V^{N-2}
$6p^2$	$^3P_0$	781 122	782 396	780 092	−0.1	−0.3
$6p^2$	$^3P_1$	7576	7710	7819	3.1	1.4
$6p^2$	$^3P_2$	10 434	10 587	10 650	2.0	0.6
$6p^2$	$^1D_2$	21 228	21 440	21 458	1.1	0.1
$6p^2$	$^1S_0$	29 779	29 808	29 467	−1.1	−1.2
$6p7p$	$^3D_1$	42 384	42 755	42 919	1.2	0.4
$6p7p$	$^3P_0$	44 017	44 299	44 401	0.9	0.2
$6p7p$	$^3P_1$	44 219	44 522	44 675	1.0	0.3
$6p7p$	$^3D_2$	44 364	44 657	44 809	1.0	0.3
$6p7s$	$^3P_0^o$	34 444	34 917	34 960	0.9	0.1
$6p7s$	$^3P_1^o$	34 778	35 243	35 287	0.9	0.1
$6p6d$	$^3F_2^o$	46 603	45 933	45 443	−0.5	−1.1
$6p6d$	$^3D_2^o$	47 176	46 756	46 061	−0.9	−1.5
$6p6d$	$^3D_1^o$	47 052	46 820	46 068	−1.0	−1.6
$6p6d$	$^3F_3^o$	47 715	47 134	46 329	−1.1	−1.7
$6p7s$	$^3P_2^o$	47 884	48 282	48 189	0.5	−0.2

core V^{N-4} potential. The virtual orbitals were obtained by solving DFS equations [36,37]. The constructed basis set included, in total, six partial waves with the orbitals up to $32s$, $32p$, $32d$, $30f$, $25g$, and $25h$ just as in the V^{N-2} case.

We used exactly the same sets of configurations for even- and odd-parity states as for the calculations in the V^{N-2} approximation discussed in previous sections. The CI + MBPT and CI + all-order methods were used as discussed in Refs. [34] and [12,51].

In Table V we compare the results obtained using the CI + all-order methods in the framework of the V^{N-2} and V^{N-4} approximations. We find that the low-lying levels belonging to the $6p^2$, $6p7p$, and $6p7s$ configurations were reproduced better in the V^{N-2} approximation. The V^{N-4} approximation gives slightly better agreement with the experiment only for the states of the $6p6d$ configuration.

We also calculated the HFS constants in the V^{N-4} approximation following the procedure described in Sec. IV B. There are no subtraction diagrams in this case. Accounting for poor initial approximation, we expect that certain corrections to the HFS constants to be large. In particular, the normalization corrections are about 6% for all HFS constants.

A comparison of the HFS constants obtained in V^{N-2} and V^{N-4} approximations using the CI + all-order method and including the RPA and other corrections, mentioned in Sec. IV B, is given in Table VI. The available experimental values are also presented. The results obtained in the V^{N-2} approximation agree with the experiment significantly better. In total, as is seen from Tables V and VI, the results obtained in the V^{N-4} approximation are generally less accurate and this method of calculation is less reliable.

TABLE VI. The magnetic dipole HFS constants (in MHz) obtained in V^{N-2} and V^{N-4} approximations are compared with the experimental values, where available. The recommended values for the V^{N-2} approximation are listed. Corresponding relative differences of these two calculations with the experimental results are given in percentages.

		CI + all			Diff. (%)	
Configuration	Term	V^{N-4}	V^{N-2}	Experiment	V^{N-4}	V^{N-2}
$6p^2$	$^3P_1$	−2265	−2392	−2389.4(0.7) [40]	5.2	−0.1
$6p^2$	$^3P_2$	2187	2513	2600.8(0.9) [40]	16	3.4
$6p^2$	$^1D_2$	453	577	609.820(8) [43]	26	5.4
$6p7p$	$^3D_1$	6062	6654			
$6p7p$	$^3P_1$	−2612	−2882			
$6p7p$	$^3D_2$	2873	3176			
$6p7s$	$^3P_1^o$	7969	8790	8802.0(1.6) [40]	10	0.14
$6p6d$	$^3F_2^o$	2678	3011	3094(9) [41]	13	2.7
$6p6d$	$^3D_2^o$	−381	−1456			
$6p6d$	$^3D_1^o$	−2388	−2884			
$6p6d$	$^3F_3^o$	1829	2079	2072(8) [41]	12	−0.4
$6p7s$	$^3P_2^o$	715	1734			

VI. CONCLUSION

In this paper we have developed and generalized the CI + all-order method for a more flexible choice of the initial approximation. Previously, using the CI + all-order method, it was needed to construct basis sets corresponding to the self-consistent field of the core. Such basis sets are not very good for the systems with several valence electrons. Here we derived coupled-cluster equations for the potential which may include (some of) valence electrons and updated our package of programs. We used this package to calculate atomic lead as a four-electron system in the V^{N-2} approximation. We studied different properties, including the energy levels, HFS constants, $E1$ transition amplitudes, and the ground-state polarizability.

For comparison we also calculated a number of Pb properties in the V^{N-4} approximation, i.e., using the self-consistent field of the core. Results of this calculation appeared to be less accurate. We conclude that for such a heavy and multivalent atom as Pb our new version of the method gives better accuracy for different observables and is more reliable.

We used this developed variant of the CI + all-order method to calculate the PNC transition amplitude $E1_{\mathrm{PNC}}\,(6p^2\ {}^3P_0\text{-}6p^2\ {}^3P_1)$. The theoretical accuracy for $E1_{\mathrm{PNC}}$ was improved by a factor of two compared to the most accurate previous calculation [31]. Using the value obtained for this amplitude and the experimental result [25,26], we found the nuclear weak charge for ^{208}Pb to be $Q_W = -117(5)$, which agrees with the SM prediction. Note that our theoretical error

(4%) is sill more than three times larger than the experimental error (1.2%). Therefore, to calculate more accurately different properties of such a heavy multivalent atom as Pb, we need further improvement of the theory. A next step in improving accuracy would be to treat SR corrections to all orders.

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APPENDIX A

The angular reduction for $U_{ij} = (U_{\mathrm{DF}} - V_{\mathrm{DF}})_{ij}$ yields

$$U_{ij} = \delta_{\varkappa_i \varkappa_j}\delta_{m_i m_j} U(ij),$$

where

$$U(ij) = \delta_{\varkappa_i \varkappa_j} \sum_{b=N_c+1}^{N_{\mathrm{DF}}} \left[\sqrt{\frac{2j_b+1}{2j_i+1}} X_0(ibjb) + \sum_L \frac{(-1)^{j_i+j_b+L}}{(2j_i+1)} X_L(bijb) \right]. \tag{A1}$$

Here the sum over index b means the sums over principal quantum number n_b and relativistic quantum number $\varkappa_b = (l_b - j_b)(2j_b+1)$, where l_b and j_b are the orbital and total angular momenta. We use notation

$$X_L(mnab) = (-1)^L \langle \varkappa_m || C^L || \varkappa_a \rangle \langle \varkappa_n || C^L || \varkappa_b \rangle R_L(mnab), \tag{A2}$$

where $R_L(mnab)$ is relativistic Slater integral and $\langle \varkappa_m || C^L || \varkappa_a \rangle$ is the reduced ME of a normalized spherical harmonic given by

$$\begin{aligned}\langle \varkappa_m || C^L || \varkappa_a \rangle &= \xi(l_m + l_a + 1)(-1)^{j_m+1/2} \\ &\quad \times \sqrt{(2j_m+1)(2j_a+1)} \begin{pmatrix} j_m & j_a & L \\ -1/2 & 1/2 & 0 \end{pmatrix},\end{aligned} \tag{A3}$$

where

$$\xi(x) = \begin{cases} 1, & \text{if } x \text{ is even}, \\ 0, & \text{if } x \text{ is odd}. \end{cases}$$

APPENDIX B

Using the formulas

$$\begin{aligned}\Sigma_{li} &= \delta_{\varkappa_l \varkappa_i}\delta_{m_l m_i} \Sigma(li), \\ \Sigma_{lnib} &= \sum_{kq} \frac{1}{\sqrt{[j_l][j_b]}} C^{j_l m_l}_{j_i m_i\, kq} C^{j_b m_b}_{kq\, j_n m_n} \Sigma_k(lnib) \\ &= \sum_{kq} (-1)^{j_i - j_n + m_i + m_n} \begin{pmatrix} j_i & k & j_l \\ m_i & q & -m_l \end{pmatrix} \\ &\quad \times \begin{pmatrix} j_b & j_n & k \\ m_b & -m_n & -q \end{pmatrix} \Sigma_k(lnib),\end{aligned}$$

we performed angular reduction in Eq. (9), arriving at

$$\begin{aligned}\Sigma(ma) &= \mathrm{LCCSD} - U(ma) + \delta_{\varkappa_m \varkappa_b} \sum_{n_b} U(ba)\rho(mb) \\ &\quad - \delta_{\varkappa_n \varkappa_a} \sum_{n_n} U(mn)\rho(na) \\ &\quad - \delta_{\varkappa_n \varkappa_b} \sum_{n_n n_b \varkappa_b} \sqrt{\frac{[j_b]}{[j_a]}} U(bn)\tilde{\rho}_0(mnab), \\ \Sigma_k(mnab) &= \mathrm{LCCSD} - \delta_{\varkappa_n \varkappa_r} \sum_{n_r} U(nr)\tilde{\rho}_k(mrab) \\ &\quad + \delta_{\varkappa_c \varkappa_b} \sum_{n_c} U(cb)\tilde{\rho}_k(mnac), \\ \Sigma(mv) &= \mathrm{LCCSD} + \delta_{\varkappa_m \varkappa_b} \sum_{n_b} \frac{U(bv)\Sigma(mb)}{\tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_b - \varepsilon_m} \\ &\quad - \delta_{\varkappa_n \varkappa_b} \sum_{n_n n_b \varkappa_b} \sqrt{\frac{[j_b]}{[j_v]}} \frac{U(bn)\tilde{\Sigma}_0(mnvb)}{\tilde{\varepsilon}_v + \varepsilon_b - \varepsilon_{mn}}, \\ \Sigma_k(mnvb) &= \mathrm{LCCSD} - \delta_{\varkappa_n \varkappa_r} \sum_{n_r} \frac{U(nr)\tilde{\Sigma}_k(mrvb)}{\tilde{\varepsilon}_v + \varepsilon_b - \varepsilon_{mr}} \\ &\quad + \delta_{\varkappa_c \varkappa_b} \sum_{n_c} \frac{U(cb)\Sigma_k(mnvc)}{\tilde{\varepsilon}_v + \varepsilon_c - \varepsilon_{mn}} \\ &\quad + \delta_{\varkappa_c \varkappa_v} \sum_{n_c} \frac{U(cv)\Sigma_k(nmbc)}{\tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_{cb} - \varepsilon_{mn}}, \\ \Sigma_k(mnvw) &= \mathrm{LCCSD} + \delta_{\varkappa_c \varkappa_w} \sum_{n_c} \frac{U(cw)\,\Sigma_k(mnvc)}{\tilde{\varepsilon}_v + \tilde{\varepsilon}_w - \varepsilon_w + \varepsilon_c - \varepsilon_{mn}} \\ &\quad + \delta_{\varkappa_c \varkappa_v} \sum_{n_c} \frac{U(cv)\,\Sigma_k(nmwc)}{\tilde{\varepsilon}_w + \tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_c - \varepsilon_{mn}},\end{aligned} \tag{B1}$$

where we use notation $[x] \equiv 2x + 1$.

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