A development of the CI + all-order method and application to the parity-nonconserving amplitude and other properties of Pb

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We have further developed and extended a method for calculation of atomic properties based on a combination of the configuration interaction and coupled-cluster approach. We have applied this approach to the 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 $6p^2\,^3P_0\rightarrow 6p^2\,^3P_1$ 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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\section{I. INTRODUCTION}

Accurate calculations 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 multi-configuration Hartree-Fock (MCHF) \cite{1,2}, relativistic multi-configuration Dirac-Fock (MCDF) \cite{3,4}, or configuration interaction (CI) \cite{5,6} methods. The core-core and core-valence correlations can be taken into account using many-body perturbation theory or coupled-cluster method \cite{7,8}.

Complexity of calculations rapidly increases with increasing number of valence electrons. Most precise calculations of different properties were carried out for monovalent atoms. In particular, parity nonconserving (PNC) amplitude for the $6s\rightarrow 7s$ transition in atomic Cs was calculated with uncertainty a few tenths of a percent \cite{11,12,13}, while the uncertainty of the PNC amplitude in the $(6s^26p)^2P_{3/2} \rightarrow (6s^26p)^2P_{1/2}$ transition of three-valence Ti is an order of magnitude larger \cite{14,15}.

The ground state electronic configuration of Pb atom is $[Xe]4f^{14}5d^{10}6s^26p^2$. Measurements of parity nonconserving optical rotation near the 1.279 $\mu$m, $6p^2\,^3P_0\rightarrow 6p^2\,^3P_1$ magnetic dipole transition in Pb were carried out almost 20 years ago by Seattle \cite{17,18} and Oxford \cite{19} 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. 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

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

where $N$ is the number of neutrons, $Z$ is the nuclear charge, and $\theta_W$ is the Weinberg angle. For $^{208}$Pb, this expression gives $Q_W \approx -120$. A more accurate standard model (SM) value, which includes radiative corrections, is $Q_W^{SM} = -118.79(5)$ \cite{20}.

Atomic parity violation studies test the standard model of the electroweak interaction by comparing the SM value of the weak charge with the $Q_W$ extracted from the experiments. 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 \cite{21,22,23}. Most accurate result for $R$ was obtained in \cite{24}, where this quantity was determined with $8\%$ uncertainty.

In this work we continue a development of the high-precision relativistic atomic method which combines the configuration interaction and coupled-cluster (CI+all-order) approaches \cite{24,25}. Initial variant of the method required either to treat Pb as a system with two valence electrons and use $V^{N-2}$ potential, or as a four-electron system using $V^{N-4}$ potential.

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. New variant of the method allowed us to consider Pb as a system with four valence electrons but use $V^{N-2}$ potential. This requires to add a number of so-called “subtraction” terms into the all-order equations. We report both $V^{N-2}$ and $V^{N-4}$ calculations of Pb proper-
ties and conclude that the former is more reliable and accurate. We calculated the quantity \( R \) to be \( R = 10.6(4) \times 10^{-8} \, i(-Q/|R|) \), reducing its uncertainty by a factor of 2 in comparison with \( 23 \).

The paper is organized as follows. In Section II we describe main features of our method and discuss a choice of initial approximation. In Sections III and IV we show how the equations, describing core-valence correlations, are modified for a more flexible choice of the potential. In Sections V and VI we discuss and compare the results obtained in \( V^{N-1} \) and \( V^{N-2} \) 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 \( H = H_0 + V \) [26, 27]:

\[
H_0 = \sum_i \varepsilon_i \{ a_i^\dagger a_i \},
\]

\[
V = \frac{1}{2} \sum_{ijkl} g_{ijkl} \{ a_i^\dagger a_j^\dagger a_k a_l \} + \sum_i (V_{DF} - U_{DF})_{ij} \{ a_i^\dagger a_j \}.
\]

Here, \( a_i^\dagger \) and \( a_i \) are the creation and annihilation operators, respectively; \{ \} designates normal form of operators in respect to the core state \( \Psi_c \); \{ \} \( \Psi_c \) = 0, and the indexes \( i, j, k, \) and \( l \) range over all possible single-electron states. \( H_0 = T + U_{DF} \) is the Hartree-Fock-Dirac (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:

\[
g_{ijkl} = \frac{1}{2} \sum_{ij} \sum_{ijkl} g_{ijkl} \{ a_i^\dagger a_j^\dagger a_k a_l \} + \frac{1}{2} \sum_{ijkl} \{ a_i^\dagger a_j^\dagger a_k a_l \}.
\]

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 DF potential for \( N_{DF} \) electrons:

\[
(U_{DF})_{ij} = \sum_{b=1}^{N_{DF}} g_{ibjb}.
\]

For monovalent atoms the natural choice is \( N_{DF} = N_c = N - 1 \), which leads to \( U_{DF} = V_{DF} \). 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 \( N_{DF} > N_c \). The dominant configuration of Pb ground state is \([\ldots]6s^26p^2\), thus Pb can be considered as an atom with 4 valence electrons. However, we can include two 6s electrons, forming closed sub-shell, in the initial HFD self-consistency procedure and construct the basis set in \( V^{N-2} \) approximation. Then the number of the core electrons is \( N_c = N - 4 \), while \( N_{DF} = N - 2 > N_c \). As a result, there will be only partial cancellation of the terms determined by the potential \( V_{DF} \) and the Dirac-Fock field \( U_{DF} \) in Eq. [3].

We designate the difference between \( V_{DF} \) and \( U_{DF} \) as \( U \). Then, for a single-electron matrix element:

\[
U_{ij} = (U_{DF} - V_{DF})_{ij}.
\]

Performing angular reduction yields:

\[
U_{ij} = \delta_{\kappa_i \kappa_j} \delta_{m_i m_j} U(ij),
\]

where

\[
U(ij) = \delta_{\kappa_i \kappa_j} \sum_{b=1}^{N_{DF}} \{ (2j_i + 1) X_L(bij) \}.
\]

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

\[
X_L(mnab) = (-1)^L \langle \kappa_m C^L | \kappa_a \rangle \langle \kappa_m C^L | \kappa_b \rangle R_{L}(mnab),
\]

where \( R_{L}(mnab) \) is relativistic Slater integral and \( \langle \kappa_m C^L | \kappa_a \rangle \) is the reduced matrix element of a normalized spherical harmonic given by:

\[
\langle \kappa_m C^L | \kappa_a \rangle = \xi(l_m + l_a + 1)(-1)^{j_m + 1/2} \times \sqrt{(2j_m + 1)(2j_a + 1)} \left( \begin{array}{ccc} j_m & j_a & L \\ -1/2 & 1/2 & 0 \end{array} \right),
\]

where

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

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 [28]:

\[
H_{\text{eff}}(E_n) \Phi_n = E_n \Phi_n,
\]

(10)
where the effective Hamiltonian is defined as

\[ H_{\text{eff}}(E) = H_{\text{FC}} + \Sigma(E), \tag{11} \]

with \( H_{\text{FC}} \) 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 many-body perturbation theory in the CI+MBPT approach \[28\] or linearized coupled cluster single-double (LCCSD) method in the CI+all-order approach \[23\].

It is convenient to decompose the effective Hamiltonian \( H_{\text{eff}}(E) \) into two parts \( H_{\text{eff}}(E) = H_1 + H_2 \), 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 \[28\].

The energy-dependent operator \( \Sigma \) is also separated into two parts, \( \Sigma = \Sigma_1 + \Sigma_2 \), where \( \Sigma_1 \) and \( \Sigma_2 \) describe one- and two-body parts of core-valence correlations, respectively. The expressions for single-electron matrix elements of these operators, \( \langle i_j | \Sigma_1 | i_j \rangle \) and \( \langle i_j k | \Sigma_2 | i_j k \rangle \), obtained in the LCCSD method approximation for the case \( U = 0 \) (i.e., when \( U_{DF} = V_{DF} \)), are given and discussed in detail in Ref. \[23\].

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:

\[
\begin{align*}
\Sigma_{ma} &= LCCSD - U_{ma} + \sum_b \rho_{mb} U_{ba} - \sum_n \rho_{na} U_{mn} - \sum_{bn} \rho_{mnab} U_{bn}, \tag{12a} \\
\Sigma_{mnab} &= LCCSD - \sum_r \tilde{\rho}_{mra} U_{ar} + \sum_c \tilde{\rho}_{mnac} U_{cb}, \tag{12b} \\
\Sigma_{mv} &= LCCSD + \sum_b \frac{\Sigma_{mb} U_{bv}}{\varepsilon_v - \varepsilon_a - \varepsilon_m - \varepsilon_n} - \sum_{bn} \frac{\tilde{\Sigma}_{mnb} U_{bn}}{\varepsilon_v + \varepsilon_b - \varepsilon_m}, \tag{12c} \\
\Sigma_{mnva} &= LCCSD - \sum_r \frac{\tilde{\Sigma}_{mrab} U_{ar}}{\varepsilon_a - \varepsilon_m + \varepsilon_v + \varepsilon_c - \varepsilon_m} + \sum_c \frac{\Sigma_{mnac} U_{ca}}{\varepsilon_v - \varepsilon_c - \varepsilon_m} + \sum_c \frac{\Sigma_{mnac} U_{cv}}{\varepsilon_v - \varepsilon_c - \varepsilon_m}, \tag{12d} \\
\Sigma_{mnvw} &= LCCSD + \sum_c \left( \frac{\Sigma_{mnva} U_{cw}}{\varepsilon_v + \varepsilon_w - \varepsilon_w + \varepsilon_c - \varepsilon_m} + \frac{\Sigma_{mnac} U_{cv}}{\varepsilon_v + \varepsilon_w - \varepsilon_v + \varepsilon_c - \varepsilon_m} \right), \tag{12e}
\end{align*}
\]

where \( \Sigma_{ij} \equiv \langle i_j | \Sigma_1 | i_j \rangle \), \( \Sigma_{ijkl} \equiv \langle i_j k | \Sigma_2 | i_j k \rangle \), and \( \varepsilon_i \) are one-electron Dirac-Fock energies and we use notation \( \varepsilon_{ij} \equiv \varepsilon_i + \varepsilon_j \). The symbol tilde over \( \varepsilon_v, \varepsilon_w \) reflects the fact that the effective Hamiltonian \[11\] is energy dependent \[23\]. A definition of the tided energy depends on the choice of initial approximation and will be discussed in Sec. \[V\].

The terms labeled “LCCSD” in \( \Sigma_{mv}, \Sigma_{mnva}, \) and \( \Sigma_{mnvw} \) are given by the right hand sides of Eqs. (22-24) in Ref. \[23\]. The core amplitudes \( \Sigma_{ma} \) and \( \Sigma_{mnab} \) are obtained from the core coefficients \( \rho_{ma} \) and \( \rho_{mnab} \) (given, for example, in \[29\]) using simple relations

\[
\begin{align*}
\Sigma_{ma} &= \rho_{ma} (\varepsilon_a - \varepsilon_m), \\
\Sigma_{mnab} &= \rho_{mnab} (\varepsilon_a + \varepsilon_b - \varepsilon_m - \varepsilon_n). \tag{13}
\end{align*}
\]

It is easy to verify that the expressions for \( \Sigma_{mnva} \) and \( \Sigma_{mnvw} \) 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.

\[\text{IV. ANGULAR REDUCTION}\]

Using the formulas

\[
\begin{align*}
\Sigma_{li} &= \delta_{\lambda l} \delta_{\mu m}, \Sigma(l_i), \\
\Sigma_{lnib} &= \sum_{kj} \frac{1}{\sqrt{|j|}} \frac{1}{\sqrt{|b|}} C_{ljm} C_{ljm} \Sigma_{knib} \tag{14a} \\
\Sigma_{lnib} &= \sum_{kj} (-1)^{j_k - j_n + m_n} \left( \begin{array}{c} j_i k_j \\ m_i q - m_l \end{array} \right) \Sigma_{knib}, \tag{14b}
\end{align*}
\]

we performed angular reduction, arriving at
\[
\Sigma(ma) = \text{LCCSD} - U(ma) + \delta_{\kappa_a,\kappa_b} \sum_{n_b} U(ba) \rho(mb) - \delta_{\kappa_a,\kappa_a} \sum_{n_a} U(mn) \rho(na) \\
- \delta_{\kappa_a,\kappa_b} \sum_{n_a,n_b,\kappa_b} \sqrt{\left| j_b \right|^2} U(bn) \hat{\rho}_0(mnab),
\]
\[
\Sigma_k(mnab) = \text{LCCSD} - \delta_{\kappa_a,\kappa_b} \sum_{n_r} U(nr) \hat{\rho}_k(mrab) + \delta_{\kappa_a,\kappa_b} \sum_{n_c} U(cb) \hat{\rho}_k(mnac),
\]
\[
\Sigma(mv) = \text{LCCSD} + \delta_{\kappa_a,\kappa_b} \sum_{n_b} \frac{U(be) \Sigma(mb)}{\tilde{\varepsilon}_b - \varepsilon_b - \varepsilon_m} - \delta_{\kappa_a,\kappa_b} \sum_{n_b,n_3,b} \sqrt{\left| j_3 \right|^2} U(bn) \tilde{\Sigma}_0(mvb),
\]
\[
\Sigma_k(mnve) = \text{LCCSD} - \delta_{\kappa_a,\kappa_b} \sum_{n_r} \frac{U(nr) \Sigma_k(mrve)}{\tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_{mr} - \varepsilon_m} + \delta_{\kappa_a,\kappa_b} \sum_{n_c} \frac{U(cb) \Sigma_k(mnvc)}{\tilde{\varepsilon}_v - \varepsilon_v + \varepsilon_c - \varepsilon_m},
\]
\[
\Sigma_k(mnvw) = \text{LCCSD} + \delta_{\kappa_a,\kappa_b} \sum_{n_c} \frac{U(cw) \Sigma_k(mnvw)}{\tilde{\varepsilon}_w - \varepsilon_w + \varepsilon_{cw} - \varepsilon_m} + \delta_{\kappa_a,\kappa_b} \sum_{n_c} \frac{U(cw) \Sigma_k(mnvw)}{\tilde{\varepsilon}_w - \varepsilon_w + \varepsilon_c - \varepsilon_m},
\]

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

V. \(V^{N-2}\) APPROXIMATION

In this section we describe a construction of the basis set and calculation of the low-lying energy levels, hyperfine structure (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 Dirac-Fock equations (disregarding the Breit interaction) for the \([1s^2,\ldots,5d^{10},6s^2]\) closed shells:

\[
\hat{H}_0 \psi_c = \varepsilon_c \psi_c,
\]

where \(\hat{H}_0\) is the relativistic DF Hamiltonian and \(\psi_c\) and \(\varepsilon_c\) 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 7s, 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 [30, 31]. The resulting basis set includes the Dirac-Fock functions for the occupied core and valence orbitals and the Dirac-Fock-Sturm 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 4-valence atom. We construct the set of configurations that contains single and double excitations of the electrons 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) using the conventional CI method, (ii) in the framework of the approach combining CI with the second order of many-body perturbation theory (CI+MBPT method [28]), and (iii) using the CI method combined with linearized coupled cluster single-double method (CI+all-order approach [24]) modified as discussed in Sec. III.

Calculations at the CI+MBPT and CI+all-order stages require knowledge of matrix elements of the operator \(\Sigma\). We emphasize that for the \(V^{N-2}\) approximation \(N_{DF} > N_c\) and \(U \neq 0\) and the modified equations (14) 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 energy levels, an energy dependence of the effective

\[
\tilde{\varepsilon}_v = \varepsilon_{v0} - U_{v0v0},
\]


Table I: \( V^{N-2} \) approximation. Theoretical and experimental \[32\] 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 4 ionization potentials (IPs): \( \text{IP}(\text{Pb}) + \text{IP}(\text{Pb}^2+) + \text{IP}(\text{Pb}^3+) + \text{IP}(\text{Pb}^4+) \). 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 2nd column the electronic terms from the NIST database \[32\] are listed. In the 3rd column the electronic terms obtained in this calculation are given, when they differ from the NIST’s ones. In the columns 4-6 we give the Landé \( g \) factors for the present calculation, \( LS \)-coupling scheme, and the experiment.

| Conf | Term | NIST | Present | \( g \) factor | CI | CI+MBPT | CI+All | Exper. | Differences (%) |
|------|------|------|---------|----------------|-----|----------|--------|--------|-----------------|
| \( 6p^2 \) | \( 3P_x \) | | | 756855 | 780823 | 782396 | 780092 | 3.0 | 0.5 | -0.2 |
| \( 6p^2 \) | \( 3P_y \) | | | 1.499 | 1.500 | 1.501 | 7093 | 7697 | 7710 | 7819 | 9.3 | 1.6 | 1.4 |
| \( 6p^2 \) | \( 3P_z \) | | | 1.277 | 1.500 | 1.269 | 9913 | 10585 | 10587 | 10650 | 6.9 | 0.6 | 0.6 |
| \( 6p^2 \) | \( 1D_2 \) | | | 1.223 | 1.000 | 1.230 | 19965 | 21401 | 21440 | 21458 | 7.0 | 0.3 | 0.1 |
| \( 6p^2 \) | \( 1S_0 \) | | | | 29084 | 29707 | 29808 | 29467 | 4.7 | -0.8 | -1.2 |
| \( 6p7p \) | \( 3P_1 \) | \( ^3D_1 \) | 0.671 | 0.500 | 40732 | 42528 | 42755 | 42919 | 5.1 | 0.9 | 0.4 |
| \( 6p7p \) | \( 3P_0 \) | | | 42303 | 44059 | 44299 | 44401 | 4.7 | 0.8 | 0.2 |
| \( 6p7p \) | \( 3P_1 \) | \( ^3P_1 \) | 1.469 | 1.500 | 42486 | 44299 | 44522 | 44675 | 4.9 | 0.8 | 0.3 |
| \( 6p7p \) | \( 3P_2 \) | \( ^3D_2 \) | 1.173 | 1.167 | 42630 | 44388 | 44567 | 44809 | 4.9 | 0.8 | 0.3 |
| \( 6p7s \) | \( 3P_0 \) | \( ^1P_1 \) | | | 33104 | 34634 | 34917 | 34960 | 5.3 | 0.9 | 0.1 |
| \( 6p7s \) | \( 3P_1 \) | \( ^1P_1 \) | | | 1.350 | 1.500 | 1.349 | 33451 | 34959 | 35243 | 35287 | 5.2 | 0.9 | 0.1 |
| \( 6p6d \) | \( 3F_2 \) | \( ^1D_2 \) | | | 0.790 | 0.667 | 0.796 | 43818 | 45660 | 45933 | 45443 | 3.6 | -0.5 | -1.1 |
| \( 6p6d \) | \( 3D_2 \) | \( ^1P_1 \) | | | 1.254 | 1.167 | 1.247 | 44631 | 46458 | 46756 | 46061 | 3.1 | -0.9 | -1.5 |
| \( 6p6d \) | \( 3D_0 \) | \( ^3P_1 \) | | | 0.883 | 0.500 | 0.864 | 44714 | 46515 | 46820 | 46068 | 2.9 | -1.0 | -1.6 |
| \( 6p6d \) | \( 3F_2 \) | \( ^3P_1 \) | | | 1.122 | 1.083 | 1.116 | 45187 | 46824 | 47134 | 46329 | 2.5 | -1.1 | -1.7 |
| \( 6p7s \) | \( 3P_2 \) | \( ^1P_3 \) | | | 1.486 | 1.500 | 1.496 | 45629 | 47959 | 48282 | 48189 | 5.3 | 0.5 | -0.2 |

where \( U_{v_0v_0} \) can be obtained from Eq. (6). Effectively, this means that we choose \( \tilde{e}_v \) to be the DF energy of the lowest valence orbital for the given partial wave in the \( V^{N-1} \) 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 a few tenth 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 experimental energy levels at the CI+all-order stage is difficult. Both methods underestimate transition energies to the levels of the \( 6p6d \) 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 \[32\] for two electronic terms. In the second column we present the electronic terms provided by NIST \[32\]. In the third column we give our assignment when it differs from the NIST terms. In the 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 \( 3P_1 \) triplet, when the levels with smaller \( J \) are lying lower (see, e.g., the book of Sobelman \[33\]). New term assignments are in agreement with this rule.

B. Hyperfine structure constants

Our goal is to calculate the \( E1 \) PNC amplitude, which is sensitive to 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 hyperfine structure constants \( A \) for the even- and odd-parity low-lying states. We calculate the \( E1 \) PNC amplitude for the zero spin isotope \( ^{208}\text{Pb} \), which was used in the experiments \[17, 19\]. Our results for the HFS constants correspond to the \( ^{207}\text{Pb} \) isotope that has nuclear spin \( I = 1/2 \) and the magnetic moment \( \mu / \mu_N \approx 0.5783 \[34\] \), where \( \mu_N \) is the nuclear magneton.

For an accurate calculation of the HFS constants we take into account not only random-phase approximation...
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 third and fourth columns, correspondingly. The remaining columns give various corrections described in the text. Values labeled “Total” are obtained as $A(\text{CI+All}) + \text{RPA} + \text{Sbt} + \sigma + \text{SR} + \text{Norm}$. The recommended values, labeled as “Recomm.”, are obtained as $A(\text{CI+All}) + \text{RPA} + \text{Sbt} + \sigma + (1/2)\text{SR} + \text{Norm}$ (see an explanation in the text). Last three columns are the experimental results available in the literature.

|       | CI | CI+MBPT | CI+All | RPA | Sbt | $\sigma$ | SR | Norm | Total | Recomm. | Refs. [35, 36] | Ref. [37] | Ref. [34] |
|-------|----|---------|-------|-----|-----|---------|----|------|-------|----------|----------------|-----------|---------|
| $6p^2 \ 3P_1$ | -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) |
| $6p^2 \ 3D_2$ | 481 | 499 | 519 | 139 | -2 | -7 | -121 | -11 | 518 | 577 | 620(6) | 609.820(8) |
| $6p^7p \ 3P_1$ | 5914 | 6635 | 6649 | 434 | -24 | -271 | -83 | -92 | 6614 | 6564 |
| $6p^7p \ 3D_1$ | -2536 | -2886 | -2888 | -181 | 11 | 122 | 27 | 39 | -2868 | -2882 |
| $6p^7p \ 3D_2$ | 2811 | 3144 | 3154 | 227 | -9 | -128 | -47 | -44 | 3153 | 3176 |
| $6p^7s \ 3P_1^0$ | 7785 | 8536 | 8528 | 632 | 121 | -329 | -74 | -123 | 8753 | 8790 | 8819(14) | 8802.0(1.6) |
| $6p^6d \ 3F_2^o$ | 2633 | 2989 | 2998 | 205 | -5 | -120 | -42 | -45 | 2990 | 3011 | 3094(9) |
| $6p^6d \ 3D_2^o$ | -827 | -1482 | -1482 | -94 | 13 | 65 | 17 | 33 | -1448 | -1456 |
| $6p^6d \ 3D_1^o$ | -2462 | -2808 | -2816 | -156 | 68 | 120 | -10 | 41 | -2889 | -2884 |
| $6p^6d \ 3F_3^o$ | 1779 | 1993 | 2000 | 140 | 81 | -82 | -27 | -44 | 2066 | 2079 | 2072(8) |
| $6p^7s \ 3P_2^0$ | 1336 | 1593 | 1604 | 287 | -40 | -43 | -94 | -26 | 1688 | 1734 |

(RPA) corrections but also the corrections beyond RPA, including one- and two-particle subtraction contributions (their sum is labeled as “Sbt”), the core-Brueckner ($\sigma$), structural radiation (SR), and normalization (Norm) corrections. 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., $A(\text{Total}) = A(\text{CI+All}) + \text{RPA} + \text{Sbt} + \sigma + \text{SR} + \text{Norm}$. 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” $H_{\text{hfs}}$ 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 2nd order of the MBPT. Usually the 2nd 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., $A(\text{Recomm.}) = A(\text{CI+All}) + \text{RPA} + \mathrm{Sbt} + \sigma + (1/2)\text{SR} + \text{Norm}$. 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 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.

Our recommended values for the HFS constants show better agreement with the experimental results [34, 37]. Note that the experimental values [35, 36] are less accurate. Moreover, their value for the $6p^2 \ 3P_2^0$ level disagrees both with the experiment [34] and with our calculation. Therefore, we do not rely on this experimental result in estimating the accuracy of our value for the HFS $6p^2 \ 3P_2^0$ 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 2nd order of the perturbation theory) involves also the matrix elements 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 $6p^2 \ 3P_0 \to 6p^2 \ 3P_1$ transition. We also calculated the value of the $6p^2 \ 3P_0$ ground state static polarizability.

For the $E1$ matrix elements, 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 matrix elements. These values are obtained in the same way as above: $D(\text{Total}) = D(\text{CI+All}) + \text{RPA} + \mathrm{Sbt} + \sigma + \text{SR} + \text{Norm}$, where $D \equiv$...
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 Ref. [39] and Ref. [40] for the \( \langle 6p^2 \,^3P_0 | d | 6p7s \,^3P_0^o \rangle \) matrix element is about 12%. For two transitions our calculated values agree with the experiment, taking into account their error bars. However, for the transition \( 6p^2 \,^3P_0 - 6p6d \,^3D_7^o \) 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. [41].

TABLE III: \( \nu^{N-2} \) approximation. The reduced matrix elements \( |\langle f|d|i\rangle| \) (in a.u.) for the electric-dipole transitions, obtained in the CI+all-order approximation and including RPA, Sbt, \( \sigma \), SR, and normalization corrections. In last column the matrix elements 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 | Experim. |
|------------|-----------|-----------|
| \( 6p^2 \,^3P_1 - 6p7s \,^3P_0^o \) | 1.89 | 2.04(7)a |
| \( 6p^2 \,^3P_0 - 6p7s \,^3P_0^o \) | 1.32 | 1.37(4)b |
| \( 6p^2 \,^3P_0 - 6p6d \,^3D_7^o \) | 2.01 | 1.62(4)c |
| \( \alpha(6p^2 \,^3P_0) \) | 46.5 | 47(7)d |

*aRef. [31]; bRef. [42]; cRef. [40]; dRef. [41].

D. PNC amplitude

The parity-nonconserving nuclear spin-independent part of electron-nuclear interaction can be written as follows:

\[
H_{PNC} = - \frac{G_F}{2\sqrt{2}} Q_W \gamma_5 \rho(r),
\]

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), \( \gamma_5 \) is the Dirac matrix, and \( \rho(r) \) is the nuclear density distribution.

We assume that the nucleus is a uniformly charged ball:

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

where \( \Theta(R - r) \) is the Heaviside step function. The root-mean-square (rms) charge radius for \( ^{208} \text{Pb} \) was measured to be \( R_{rms} = 5.5010 \text{ fm} \) [43]. Using the formula \( R = \sqrt{5/3} R_{rms} \), we find \( R \approx 7.1108 \text{ fm} \).

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:

\[
|\langle f|d_{PNC}|i\rangle| = \sum_n \left[ \frac{|\langle f|d_q|n\rangle| |H_{PNC}|i\rangle|}{E_i - E_n} + \frac{|\langle f|H_{PNC}|n\rangle| |d_q|i\rangle|}{E_f - E_n} \right].
\]

For two transitions our calculated values agree with the experimental result, 47(7) a.u. [41].

\[ E_{1PNC} \equiv |\langle f|d_{PNC}|i\rangle| \]

\[
= \sum_n \left( \frac{\langle 3P_1|d|n\rangle |H_{PNC}|3P_0 \rangle}{E_{p0} - E_n} + \frac{\langle 3P_1|H_{PNC}|n\rangle |d|3P_0 \rangle}{E_{p0} - E_n} \right)
\]

\[ = E_{1PNC}^{(1)} + E_{1PNC}^{(2)}. \]

Introducing notations

\[
|\delta\psi_1\rangle = \sum n |n\rangle |H_{PNC}|3P_0 \rangle / E_{p0} - E_n,
\]

\[
|\delta\psi_2\rangle = \sum n \langle 3P_1|H_{PNC}|n\rangle |n\rangle / E_{p0} - E_n,
\]

we express \( E_{1PNC}^{(1)} \) and \( E_{1PNC}^{(2)} \) as

\[
E_{1PNC}^{(1)} = \langle 3P_1|d|\delta\psi_1\rangle,
\]

\[
E_{1PNC}^{(2)} = \langle \delta\psi_2|d|3P_0 \rangle.
\]

The \( E_{1PNC} \) amplitude is sensitive to the matrix elements of the weak interaction \( H_{PNC} \), \( E1 \) 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 matrix elements 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, structural radiation, and normalization corrections, as we did when calculated the HFS constants.
The breakdown of different contributions to the terms \( E_{1,1}^{(1)} \) and \( E_{1,1}^{(2)} \) determined by Eq. (19) (in a.u.). The values of \( M_1 \equiv \langle 6p^2 \, 3P_0 | |\mu| |6p^2 \, 3P_0 \rangle \) are in the Bohr magnetons. The values of \( R \) are given in units \( 10^{-8} \times (Q_W/N) \).

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 \((\text{CI+All})+\text{RPA}+\sigma+\text{SR}+\text{Sbt}+\text{Norm}\). Numbers labeled “Recomm.” are obtained as \((\text{CI+All})+\text{RPA}+\sigma+(1/2)\text{SR}+\text{Sbt}+\text{Norm}\) (see the explanation in the text).

| Term | \( E_{1,1}^{(1)} \) | \( E_{1,1}^{(2)} \) | \( M_1 \) | \( R \) |
|------|------------------|------------------|--------|--------|
| CI   | 2.619            | 2.109            | -1.297 | -0.99  |
| 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  |
| \( \sigma \) | -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)*        | -11.4b           | -13.1c |

*Ref. 23; *Ref. 22; *Ref. 21.

When the \( E_{1,1}^{(1)} \) amplitude transition is obtained, we are able to find the quantity

\[
R = \frac{\text{Im}(E_{1,1}^{(1)})}{M_1},
\]

where we take into account that \( E_{1,1}^{(1)} \) is imaginary and designate the reduced matrix element of the magnetic dipole operator \( \mu \): \( M_1 \equiv \langle 6p^2 \, 3P_0 | |\mu| |6p^2 \, 3P_0 \rangle \). The quantity \( R \) was experimentally determined in [17, 18], so we are able to compare theory and experiment.

The results of calculation of both \( E_{1,1}^{(1)} \) and \( E_{1,1}^{(2)} \) terms, determined by Eq. (19), are presented in Table IV. Our analysis shows that the intermediate state \( 6p^7s \, 3P_0 \) gives dominating (\( \sim 86\% \)) contribution to \( E_{1,1}^{(1)} \). Thus, the contribution of higher-lying states is rather small.

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

Such anomalously large contribution comes from the higher-lying odd-parity states belonging to the configuration \( 6s \, 6p^5 \). According to our calculation the lowest state with \( J = 1 \), belonging to this configuration, is lying \( \sim 74000 \text{ cm}^{-1} \) above the ground state. The ma-

trix elements of the electric dipole and \( H_{PNC} \) operators are large: \( \langle 6s^2 \, 6p^2 \, 3P_0 \rangle |D|6s^2 \, 6p^2 \, 3P_0 \rangle = 1.91 \text{ a.u.} \) and \( \langle 6s^2 \, 6p^3 \, J = 1 |H_{PNC}|6s^2 \, 6p^2 \, 3P_0 \rangle = 476 \text{ a.u.} \). As a result, the contribution of this odd-parity state to \( E_{1,1}^{(2)} \) is large and positive.

It is worth noting that, for the reason discussed above, a direct summation over intermediate states is not applicable for calculation of \( E_{1,1}^{(2)} \). Instead, we solve inhomogeneous equation [43] which accounts for contribution from all discrete states and a continuum.

Analyzing the RPA and other corrections to \( E_{1,1}^{(1)} \) and \( E_{1,1}^{(2)} \), 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 \( E_{1,1}^{(1)} + E_{1,1}^{(2)} \). For this reason the role of smaller corrections (\( \sigma \), Sbt, etc.) is enhanced.

A procedure of including the RPA, \( \sigma \), and SR corrections in calculating \( E_{1,1}^{(1)} \) is reduced to “dressing” the \( H_{PNC} \) and \( \mathbf{d} \) operators, as described in detail in [38]. To find the subtraction and normalization corrections, following the recipe of Ref. 38, we obtained \( |\delta \psi_1 \rangle \) and \( |\delta \psi_2 \rangle \), given by Eq. (20), for the effective operator \( H_{PNC}^{eff} \) and then calculated the MEs in (21) for the effective electric dipole operator \( \mathbf{d}^{eff} \).

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, \( \sigma \), Sbt, and Norm. As we discussed above, the SR corrections turn out to be overestimated in the 2-n.d 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 \( E_{1,1}^{(1)} \) less than 0.1% and we neglect this contribution.

The RPA and other similar corrections are very small for the \( M_1 \) matrix element \( \langle 6p^2 \, 3P_1 | |\mu| |6p^2 \, 3P_0 \rangle \) and can be neglected without loss of accuracy. We present the values of the quantity \( R \) (given by Eq. (22)) obtained in different approximations in the last column of the table. Various corrections to \( R \) are listed as well. Our recommended value is \( R = -10.6(4) \times 10^{-8} \times (Q_W/N) \). Based on the calculation accuracy of the HFS constants, \( E_1 \) transition amplitudes, and the ground state polarizability, we assign to the quantity \( R \) the uncertainty \( \sim 4\% \). Our result is in a good agreement with earlier calculations [21, 22] but the accuracy is two times higher.

Using our recommended value of \( R \) and the most accurate experimental value \( -9.86 \pm 0.12 \times 10^{-8} \) [17, 18] we find the weak nuclear charge for \( ^{208}\text{Pb} \) to be \( Q_{W} = -117(5) \). This value is in good agreement with the SM prediction \( Q_{SM}^{W} = -118.79(5) \) [21]. Note that our theo-
retical 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.

VI. VN-4 APPROXIMATION

It is worth noting that due to importance of the 6s6p3 configuration for the E1PNC amplitude discussed above, a two-electron calculation of Pb using VN-2 approximation gives poor results. In this section, as earlier, we consider Pb as the 4-valence atom using VN-4 approximation and compare results with those obtained previously in the VN-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 Dirac-Fock-Sturm approach, but the Dirac-Fock equations were solved for the [1s2, ..., 5d10] 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 core VN-4 potential. The virtual orbitals were obtained by solving Dirac-Fock-Sturm equations [30, 31]. The constructed basis set included, in total, 6 partial waves with the orbitals up to 32s, 32p, 32d, 30f, 25g and 25h just as in the VN-4 case.

TABLE V: The energy levels (in cm−1) obtained using the CI+all-order method in VN-2 and VN-4 approximations are compared with the experiment [32]. 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 2nd column correspond to the new assignment discussed in text.

| Conf. Term | CI+All VN-4 | V N-2 | Exp. | Diff. (%) VN-4 | VN-2 |
|------------|-------------|-------|------|---------------|------|
| 6p2 3P0    | 781122      | 782396 | 780092 | -0.1          | -0.3 |
| 6p2 3P1    | 7576        | 7710   | 7819  | 3.1           | 1.4  |
| 6p2 3P2    | 10434       | 10587  | 10650 | 2.0           | 0.6  |
| 6p2 1D2    | 21228       | 21440  | 21458 | 1.1           | 0.1  |
| 6p2 1S0    | 29779       | 29908  | 29467 | -1.1          | -1.2 |
| 6p7p 3P1   | 42384       | 42755  | 42919 | 1.2           | 0.4  |
| 6p7p 3P2   | 44017       | 44299  | 44401 | 0.9           | 0.2  |
| 6p7p 3P3   | 44219       | 44522  | 44675 | 1.0           | 0.3  |
| 6p7p 3P4   | 44364       | 44657  | 44809 | 1.0           | 0.3  |
| 6p7s 3P0   | 34444       | 34917  | 34960 | 0.9           | 0.1  |
| 6p7s 3P1   | 34778       | 35243  | 35287 | 0.9           | 0.1  |
| 6p7s 3P2   | 46603       | 45933  | 45443 | -0.5          | -1.1 |
| 6p7s 3P3   | 47715       | 47134  | 46329 | -1.1          | -1.7 |
| 6p7s 3P4   | 47884       | 48282  | 48189 | 0.5           | -0.2 |

We used exactly the same sets of configurations for even- and odd-parity states as for the calculations in the VN-2 approximation discussed in previous sections. The CI+MBPT and CI+all-order methods were used as discussed in Refs. [28] and [24, 25].

In Table VI we compare the results obtained using the CI+all-order methods in the framework of the VN-2 and VN-4 approximations. We find that the low-lying levels belonging to the 6p2, 6p7p, and 6p7s configurations were reproduced better in the VN-2 approximation. The VN-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 VN-4 approximation following the procedure described in Section VI. 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.

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

| Conf. Term | CI+All VN-4 | VN-2 | Experiment | Diff. (%) VN-4 | VN-2 |
|------------|-------------|-------|------------|---------------|------|
| 6p2 3P0    | -2265       | -2392 | -2389.4    | 5.2           | -0.1 |
| 6p2 3P1    | 2187        | 2513  | 2506.8     | 16            | 3.4  |
| 6p2 3D2    | 453         | 577   | 609.820    | 26            | 5.4  |
| 6p7p 3P1   | -2612       | -2882 | 1          | 10            | 0.14 |
| 6p7p 3P2   | 2873        | 3176  | 5          | 13            | 2.7  |
| 6p7s 3P0   | 7969        | 8790  | 8802.0     | 13            | 2.7  |
| 6p7s 3P1   | 2678        | 3011  | 3094(9)    | 13            | 2.7  |
| 6p7s 3P2   | -381        | -1456 | 1          | 13            | 2.7  |
| 6p7s 3P3   | -2388       | -2884 | 1          | 13            | 2.7  |
| 6p7s 3P4   | 1829        | 2079  | 2072(8)    | 13            | 2.7  |

A comparison of the HFS constants obtained in VN-2 and VN-4 approximations using the CI+all-order method and including the RPA and other corrections, mentioned in Section VI.1 is given in Table VI. The available experimental values are also presented. The results obtained in the VN-2 approximation agree with the experiment significantly better. In total, as is seen from Tables V and VI the results obtained in the VN-4 approximation are generally less accurate and this method of calculation is less reliable.
VII. 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, hyperfine structure 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 parity nonconserving transition amplitude $E1_{\text{PNC}} (6p^2 \frac{3}{2}P_0 - 6p^2 \frac{3}{2}P_1)$. The theoretical accuracy for $E1_{\text{PNC}}$ was improved by a factor of two compared to the most accurate previous calculation [23]. Using the value obtained for this amplitude and the experimental result [17] $[18]$, 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 still 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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