Calculation of the energy levels of Ge, Sn, Pb and their ions in the $V^{N-4}$ approximation

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Energy levels of germanium, tin and lead together with their single, double and triple ionized positive ions have been calculated using the $V^{N-M}$ approximation suggested in the previous work (Dzuba, physics/0501032) ($M = 4$ - number of valence electrons). Initial Hartree-Fock calculations are done for the quadruply ionized ions with all valence electrons removed. The core-valence correlations are included beyond the second-order of the many-body perturbation theory. Interaction between valence electrons is treated by means of the configuration interaction technique. It is demonstrated that accurate treatment of the core-valence correlations lead to systematic improvement of the accuracy of calculations for all ions and neutral atoms.

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I. INTRODUCTION

This work further develops the $V^{N-M}$ approximation suggested in Ref. [1]. It also presents the details of the calculations of the energy levels of Ge II, Sn II and Pb II which were needed to study their dependence on the fine structure constant $\alpha$ ($\alpha = e^2/\hbar c$). Some lines of Ge II, Sn II and Pb II have been observed in quasar absorption spectra and the information on the dependence of corresponding frequencies on $\alpha$ is needed to study possible variation of the fine structure constant at early epoch.

In the vicinity of the physical value of $\alpha$ the frequency of an atomic transition can be presented in a form

$$\omega = \omega_0 + qx,$$

where $x = (\alpha/\alpha_0)^2 - 1$ and $\alpha_0$ and $\omega_0$ are the present-day laboratory values of the fine structure constant and transition frequency.

The values of the $q$-coefficients can only be found from atomic calculations by, e.g., varying the value of $\alpha$ in computer codes based on relativistic equations. In many cases calculated values of the $q$-coefficients are more stable than the energies. This is because they are not sensitive to incompleteness of the basis set with respect to the principal quantum number $n$. Indeed, relativistic corrections are proportional to $1/\nu^3$ ($\nu$ is the effective principal quantum number) while energies are proportional to $1/\nu^2$. If we include more states of high $\nu$ this would have greater effect on the energies than on relativistic corrections presented by $q$-coefficients.

However, in the case of strong configuration mixing and level pseudo-crossing calculation of $q$-coefficients may become very unstable. In the vicinity of level pseudo-crossing the values of $q$-coefficients change very rapidly with $\alpha$ and small error in determining the position of the level crossing may lead to large error in the values of $q$.

Level pseudo-crossing always means strong configuration mixing between the states. However, strong configuration mixing may also take place without level pseudo-crossing. This can also cause instability in calculated values of $q$-coefficients. Indeed, relativistic correction to the energy of a single electron state $|njlm\rangle$ strongly depends on the total momentum $j$ of this state (see, e.g., formula (7) in Ref. [2]). Therefore configurations composed from states of different $j$ may have very different values of $q$ and small error in the the configuration mixing coefficients would lead to large error in the resulting $q$ value for the mixed state.

Strong configuration mixing and level pseudo-crossing take place for Ge II, Sn II and Pb II ions as well as for many other atoms and ions. This means that calculations need to be done to very high accuracy to ensure stable values of the $q$-coefficients. The criterion is that deviation of the calculated energies from the experimental values must be much smaller than the experimental energy interval between mixed states.

There are many other areas of research where accurate atomic calculations are needed. These include parity and time invariance violation in atoms (see, e.g. [3]), interaction of positrons with atoms [4], etc.

A way to do accurate calculations for atoms with several $s$ and/or $p$ valence electrons has been suggested in Ref. [1]. It is called “the $V^{N-M}$ approximation”, where $V$ is the Hartree-Fock potential created by $N - M$ electrons of the closed shell ion, $N$ is total number of electrons in neutral atom and $M$ is the number of valence electrons. Initial Hartree-Fock calculations are done for a closed-shell positive ion with all valence electrons removed. It has been demonstrated in Ref. [1] that the Hartree-Fock potential of the closed-shell positive ion is often a good starting approximation for a neutral atom. This is the case when valence electrons are localized on distances larger than the size of the core. Then they can affect only energies of core states but not their wave functions. Since the potential created by core electrons depends on the electron charge density and does not depend on electron energies it doesn’t matter which core
The effective Hamiltonian for valence electrons is constructed using the configuration interaction (CI) technique. Core-valence correlations are included by adding the electron correlation operator \( \Sigma \) to the CI Hamiltonian. Many-body perturbation theory (MBPT) is used to calculate \( \Sigma \). The main advantage of the \( V^{N-M} \) approximation is that MBPT is relatively simple (no subtraction diagrams) and the \( \Sigma \) operator can be calculated beyond the second-order of the MBPT. It has been demonstrated in Ref. [1] that inclusion of the higher-order core valence correlations lead to further significant improvement of the accuracy of calculations. In the present work we study twelve complicated many-electron systems including germanium, tin, lead and their positive ions. We demonstrate that using the \( V^{N-M} \) approximation (\( M = 4 \) for the case of Ge, Sn and Pb) and accurate treatment of the core-valence correlations lead to high accuracy of calculations for all twelve systems. This indicates that the \( V^{N-M} \) approximation is a good approximation for a wide range of atoms and ions.

II. CALCULATIONS

The effective Hamiltonian for valence electrons in the \( V^{N-M} \) approximation has the form

\[
\hat{H}^{\text{eff}} = \sum_{i=1}^{M} \hat{h}_{1i} + \sum_{i \neq j}^{M} \hat{h}_{2ij},
\]

\( \hat{h}_{1i}(r_i) \) is the one-electron part of the Hamiltonian

\[
\hat{h}_1 = c\alpha \cdot \mathbf{p} + (\beta - 1)mc^2 - \frac{Ze^2}{r} + V^{N-M} + \Sigma_1.
\]

\( \Sigma_1 \) is the correlation potential operator which is exactly the same in the \( V^{N-M} \) approximation as for the single-valence electron atoms (see, e.g. [2]). It can be calculated in the second-order of the MBPT. Selected chains of the higher-order diagrams can be included into \( \Sigma_1 \) in all orders using technique developed for single-valence electron atoms (see, e.g. [10]).

\( \hat{h}_2 \) is the two-electron part of the Hamiltonian

\[
\hat{h}_2 = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \hat{\Sigma}_2(r_1, r_2),
\]

\( \hat{\Sigma}_2 \) is the two-electron part of core-valence correlations. It represents screening of Coulomb interaction between valence electrons by core electrons. We calculate \( \hat{\Sigma}_2 \) in the second order of MBPT. Inclusion of the higher-order correlations into \( \hat{\Sigma}_2 \) will be a subject of further study.

However, the calculations show that in most cases accurate treatment of \( \Sigma_1 \) is more important than for \( \Sigma_2 \). The details of the calculation of \( \Sigma_1 \) and \( \Sigma_2 \) can be found elsewhere [11, 12]. Note however that in contrast to the previous works [11, 12] we have no so called subtraction diagrams.

Number of electrons \( M \) is the only parameter in the effective Hamiltonian [2] which changes when we move between different ions of the same atom. The terms \( V^{N-M} \), \( \Sigma_1 \) and \( \Sigma_2 \) remain exactly the same.

The form of the effective Hamiltonian is also the same for all ions if some other potential \( V \) is used to generate the core states. However, the \( \Sigma \) operator would have terms proportional to \( V^{N-M} - V \) (subtraction diagrams [11]). In the \( V^{N-M} \) approximation \( V \equiv V^{n-4} \) and subtraction diagrams disappear. The MBPT becomes relatively simple which makes it easier to include higher-order core-valence correlations.

A. Electron shell structure of lead.

To understand how the \( V^{N-M} \) approximation works it is very instructive to look at electron shells of a many-electron atom. We chose lead because it is the heaviest of the considered atoms. It probably has the richest possible electron shell structure. Neutral lead has eighty two electrons occupying six shells. Angular momentum \( l \) ranges from 0 (s-electrons) to 3 (f-electrons). Figs. [4] and [2] present electron densities of Pb I (solid line) and Pb V (dotted line) separately for s, p, d and f electrons. The density is the sum over principal quantum number \( n \), total momentum \( j \) and its projection \( m \) while angular
momentum \( l \) is fixed:
\[
\rho(r)_l = \sum_{njm} |\psi(r)_{njml}|^2 r^2.
\]

The values of \( \rho(r)_l \) in the maximum are very different for different \( l \). Therefore, we present normalized functions \( \rho(r)/\rho_{\text{max}} \) to be able to fit all graphs into one diagram.

Electron shell structure can be clearly seen on Fig. 1. Each density has a local peak at \( n - l = 1, 2, \text{etc.} \) The position of the peak depends mostly on \( n \) and is about the same for all \( l \). This means that all electrons with the same \( n \) are localized at about the same distances regardless of their angular momentum \( l \), thus making a shell.

The difference between Pb I and Pb V cannot be seen on Fig. 1. Fig. 2 presents details of the right bottom corner of the Fig. 1. Dotted lines which correspond to electron densities of the Pb V ion show no peak at \( n = 6 \) because of absence of the 6s and 6p electrons. The removal of four valence electrons has some effect on the density of d-electrons at about the same distances where the 6s and 6p electrons are localized and practically no effect on the densities of all electrons on shorter distances. This is because valence electrons are localized on large distances and they can only create constant potential in the core which can change the energies of the core states but cannot change their wave functions.

One can see from Fig. 2 that there is an overlap between the wave functions of valence electrons of Pb I (6s and 6p electrons) and the wave function of the core outermost state 5d. We have presented for comparison on Fig. 3 the electron densities of Ba I and Ba III on large distances. It is easy to see that the overlap between core and valence electrons in barium is much smaller than the overlap between core and valence electrons in lead. As a consequence, outermost core state of barium (5p) is much less affected by removal of two 6s electrons than compared to the effect of removal of two 6s and two 6p electrons on the 5d state of lead. This means that the \( V^{N-2} \) approximation for Ba should work much better than the \( V^{N-4} \) approximation for Pb. The situation is exactly the same as for the \( V^{N-1} \) approximation for atoms with one external electron. It is very well known that the \( V^{N-1} \) approximation works extremely well for alkali atoms and not so well for atoms like Ga, In, Tl, etc. The reason is the same in both cases. Valence electrons must not overlap with the core for the \( V^{N-M} \) to be good starting approximation regardless of whether \( M = 1 \) or \( M > 1 \).

Similar to the fact that the \( V^{N-1} \) approximation is a good approximation for thallium, although not as good as for alkali atoms, the \( V^{N-M} \) approximation is a good approximation for Pb, Sn and Ge, although not as good as for Ba.

Below we present specifics of calculations for germanium, tin and lead.

B. Calculations for germanium

Germanium is the lightest of three atoms \((Z=32)\) and the easiest from computational point of view. Its ground state configuration is 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d\(^10\)4s\(^2\)4p\(^2\). The core-valence correlations are relatively small due to small number of electrons in the core.

We calculate \( \Sigma_1 \) and \( \Sigma_2 \) for the effective Hamiltonian in the second order of the MBPT. Inclusion of \( \Sigma_1 \) brings single-electron energies of Ge IV to agreement with the experiment on the level of 0.1%. No higher-order
core-valence correlations need to be included.

In fact, inclusion of the higher-order correlations using technique developed in Ref. [10] doesn’t lead to better results for germanium. This is because the technique was developed for heavy atoms in which higher order correlations are dominated by screening of the Coulomb interaction between core and valence electrons by other core electrons. In light atoms like germanium this effect does not dominate due to small number of electrons in the core. Therefore, inclusion of screening, while other higher-order effects are not included, does not improve the accuracy.

The results of calculations are presented in Table I. The ground-state energies are given as energies to remove all valence electrons from an atom or ion (in atomic units). Corresponding experimental energies are sums of the ionization potentials of all relevant ions. For the convenience of comparison with Moore’s tables [14] we present energies of excited states relative to the ground state in cm$^{-1}$. Column marked CI presents the results of the standard configuration interaction method without $\Sigma$. Column $\Sigma^{(2)}$ presents the results of calculations with the effective Hamiltonian $\hat{\Sigma}$ in which $\Sigma$ is calculated in the second order of MBPT.

The results presented in Table II show that inclusion of the core-valence correlations leads to systematic significant improvement of the accuracy of calculations for all states of all ions and for neutral germanium.

### C. Calculations for tin.

Tin atom ($Z = 50$) is very similar to the germanium atom. Its ground state configuration is \ldots $5s^25p^2$. However, correlations and relativistic corrections are larger. It has some implication on the calculation scheme. It turns out that inclusion of the higher-order core-valence correlations does lead to significant improvement of the results for all tin ions and for the neutral atom. We include screening of Coulomb interaction and hole-particle interaction in all orders of the MBPT in the calculation of $\Sigma_1$. It is done exactly the same way as in our calculations for single-valence-electron atoms (see, e.g. [10]). The $\Sigma_2$ operator is still calculated in the second order of the MBPT.

The results are presented in Table III. There is one more column in the table compared to Table I. It is marked $\Sigma^{(\infty)}$ and presents the results of calculations with all-order $\Sigma_1$. Again, it easy to see that moving from less sophisticated to more sophisticated approximations (with no $\Sigma$; with $\Sigma^{(2)}$; with $\Sigma^{(\infty)}$) leads to systematic significant improvement of the accuracy of the results.

### D. Calculations for lead

The case of lead ($Z = 82$) is the most difficult of the calculations. Correlations are strong and relativistic effects are large too. Strong $L - S$ interaction leads to intersection of the fine-structure multiplets. Also, states of the same total momentum $J$ are strongly mixed regardless of the values of $L$ and $S$ assigned to them. The breaking of the $L - S$ scheme can be easily seen e.g. by comparing experimental values of the Landé $g$-factors with the non-relativistic values.

We have done one more step for lead to further improve the accuracy of calculations as compared to the scheme used for tin. We have introduced the scaling fac-

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**TABLE I: Ground state removal energies (RE, a.u.) and excitation energies (cm$^{-1}$) of low states of Ge IV to Ge I.**

| State | CI | $\Sigma^{(2)}$ | Exp. [13] |
|-------|----|----------------|-----------|
| $4s_{1/2}$ | RE | -1.63631 | -1.68047 | -1.67993 |
| $4p_{1/2}$ | 78746 | 81623 | 81315 |
| $4p_{3/2}$ | 81372 | 84470 | 84103 |
| $4d_{1/2}$ | 183779 | 191142 | 190607 |
| $4d_{5/2}$ | 184049 | 191424 | 190861 |
| $4s^2$ | $1S_0$ | -2.85213 | -2.93114 | -2.93765 |
| $4s4p^2$ | $3P_0^{(3)}$ | 57762 | 61812 | 61734 |
| | $3P_1^{(3)}$ | 58490 | 62595 | 62500 |
| | $3P_2^{(3)}$ | 60030 | 64273 | 64144 |
| $4s4p^2$ | $1P_1^{(3)}$ | 90820 | 92230 | 91873 |
| $4s4d$ | $1D_2$ | 137686 | 145305 | 144975 |
| $4p^2$ | $3P_0$ | 142850 | 148023 | 147685 |
| | $3P_1^2$ | 143712 | 148997 | 148640 |
| | $3P_2$ | 145276 | 150765 | 150372 |
| $4s5s$ | $3S_1$ | 152184 | 158630 | 158565 |
| $4s^24p^2$ | $2P_{1/2}^{(3)}$ | -3.42590 | -3.51488 | -3.53222 |
| | $2P_{3/2}^{(3)}$ | 1623 | 1797 | 1767 |
| $4s^25p^2$ | $2P_{1/2}^{(3)}$ | 47667 | 51512 | 51576 |
| | $2P_{3/2}^{(3)}$ | 48326 | 52241 | 52291 |
| | $2P_{5/2}^{(3)}$ | 49333 | 53342 | 53367 |
| $4s^25s^2$ | $2S_1^{(3)}$ | 61124 | 62870 | 62402 |
| $4s^24p^2$ | $2D_{3/2}$ | 61750 | 65313 | 65015 |
| | $2D_{5/2}$ | 61930 | 65494 | 65184 |
| $4s^24d$ | $2D_{3/2}^{(3)}$ | 77370 | 79386 | 79006 |
| | $2D_{5/2}^{(3)}$ | 77710 | 79750 | 79366 |
| $4s^24p^2$ | $3P_0$ | 79270 | 81444 | 80836 |
| | $3P_1$ | 79439 | 81625 | 81012 |
| $4s^24p^2$ | $1P_1$ | 42010 | 41648 | 40020 |
| $4s^24p^5s$ | $1S_0$ | 45489 | 45503 | 45985 |
| $4s^24p5p$ | $1P_1$ | 57762 | 61812 | 61734 |
| | $3D_3$ | 46426 | 46199 | 46765 |
| | $3D_2$ | 46332 | 46275 | 46834 |
| | $3D_1$ | 47469 | 47620 | 48104 |
TABLE II: Ground state removal energies (RE, a.u.) and excitation energies (cm⁻¹) of low states of Sn IV to Sn I.

| State          | CI  | \(\Sigma^{(2)}\) | \(\Sigma^{(\infty)}\) | Exp. | [14] |
|----------------|-----|------------------|----------------------|------|------|
| 4d\(^{10}\)5s  | \(2S_{1/2}\) RE | -1.43894 | -1.51228 | -1.49776 | -1.49699 |
| 4d\(^{10}\)5p  | \(2P_{1/2}\) | 66323 | 70709 | 69727 | 69564 |
| 4d\(^{10}\)5d  | \(2D_{3/2}\) | 72291 | 77409 | 76264 | 76072 |
| 4d\(^{10}\)5d  | \(2D_{1/2}\) | 156481 | 168074 | 165406 | 165305 |
| 4d\(^{10}\)5s  | \(2D_{3/2}\) | 157180 | 168847 | 166183 | 165411 |
| Sn III         |      |                  |                      |      |      |
| 5s\(^{2}\)     | \(1S_{0}\) RE | -2.51142 | -2.64097 | -2.61447 | -2.61794 |
| 5s5p           | \(3P_{1}^{o}\) | 47961 | 54914 | 54001 | 53548 |
| 5s5p           | \(3P_{0}\) | 49548 | 56582 | 55631 | 55196 |
| 5s5p           | \(3P_{2}\) | 53207 | 60734 | 59670 | 59299 |
| 5s5p           | \(1P_{0}\) | 78801 | 80163 | 79019 | 79011 |
| 5p\(^{2}\)     | \(3P_{0}\) | 121290 | 128814 | 126873 | 127309 |
| 5p\(^{2}\)     | \(3P_{2}\) | 123690 | 131743 | 129709 | 130120 |
| 5p\(^{2}\)     | \(3P_{2}\) | 118412 | 136470 | 134275 | 134567 |
| 5p\(^{2}\)     | \(1D_{3}\) | 127379 | 130638 | 128478 | 128205 |
| 5s5s           | \(3S_{1}\) | 130986 | 141420 | 139341 | 139638 |
| 5s5d           | \(3D_{1}\) | 123760 | 142898 | 140463 | 141322 |
| 5s5d           | \(3D_{2}\) | 123946 | 143107 | 140671 | 141526 |
| 5s5d           | \(3D_{3}\) | 133222 | 143423 | 140987 | 141838 |
| 5s5s           | \(1S_{0}\) | 135453 | 145105 | 143043 | 143591 |
| 5s5d           | \(1D_{2}\) | 148378 | 155394 | 153063 | 154116 |
| Sn I           |      |                  |                      |      |      |
| 5s\(^{2}\)5p   | \(2P_{1/2}^{o}\) RE | -3.03218 | -3.17791 | -3.14624 | -3.15567 |
| 5s\(^{2}\)5p   | \(2P_{3/2}^{o}\) | 3776 | 4352 | 4222 | 4251 |
| 5s5p\(^{2}\)   | \(4P_{1/2}\) | 40839 | 47579 | 46661 | 46464 |
| 5s5p\(^{2}\)   | \(4P_{3/2}\) | 42512 | 49537 | 48556 | 48368 |
| 5s5p\(^{2}\)   | \(4P_{1/2}\) | 44720 | 51958 | 50915 | 50730 |
| 5s\(^{2}\)6s   | \(2S_{1/2}\) | 54896 | 57545 | 56707 | 56886 |
| 5s5p\(^{2}\)   | \(2D_{2}\) | 54142 | 59969 | 58806 | 58844 |
| 5s5p\(^{2}\)   | \(2D_{0}\) | 54731 | 60590 | 59419 | 59463 |
| 5s\(^{2}\)5d   | \(2D_{2}\) | 69220 | 72247 | 71140 | 71406 |
| 5s\(^{2}\)5d   | \(2D_{0}\) | 69776 | 72929 | 71804 | 72048 |
| 5s\(^{2}\)6p   | \(2P_{1/2}^{o}\) | 69006 | 72131 | 71182 | 71494 |
| 5s\(^{2}\)6p   | \(2P_{3/2}^{o}\) | 69825 | 73025 | 72061 | 72377 |
| Sn I           |      |                  |                      |      |      |
| 5s\(^{2}\)5p\(^{2}\) | \(3P_{0}\) RE | -3.28899 | -3.44213 | -3.407850 | -3.425548 |
| 5s\(^{2}\)5p\(^{2}\) | \(3P_{1}\) | 1411 | 1681 | 1623 | 1692 |
| 5s\(^{2}\)5p\(^{2}\) | \(3P_{2}\) | 3049 | 3539 | 3428 | 3428 |
| 5s\(^{2}\)5p\(^{2}\) | \(1D_{2}\) | 8359 | 9079 | 8891 | 8613 |
| 5s\(^{2}\)5p\(^{2}\) | \(1S_{0}\) | 17328 | 18217 | 17977 | 17163 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{0}\) | 35381 | 35722 | 35251 | 34641 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{1}\) | 35764 | 36050 | 35577 | 34914 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{2}\) | 38988 | 39848 | 39252 | 38629 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{1}\) | 40080 | 40655 | 40063 | 39257 |
| 5s\(^{2}\)5p\(^{3}\) | \(5S_{2}\) | 34742 | 40529 | 39725 | 39626 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{0}\) | 42805 | 44164 | 43578 | 43430 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{1}\) | 41361 | 42785 | 42200 | 42342 |
| 5s\(^{2}\)5p\(^{6}\) | \(3P_{2}\) | 45804 | 47712 | 47008 | 47235 |
| 5s\(^{2}\)5p\(^{6}\) | \(3D_{1}\) | 42356 | 43768 | 43178 | 43369 |
| 5s\(^{2}\)5p\(^{6}\) | \(3D_{2}\) | 42447 | 43861 | 43267 | 43239 |
| 5s\(^{2}\)5p\(^{6}\) | \(3D_{3}\) | 45543 | 47511 | 46796 | 47007 |

It is instructive to compare our results with recent calculations by Safronova et al. [15] (see Table III). Energy levels of Pb II were calculated by Safronova et al with the use of the coupled-cluster (CC)
approach and the third-order MBPT. The Pb II ion was treated as an ion with one external electron above closed shells. Therefore only energies of states in which the 6s subshell remained closed were calculated. The agreement with experiment for these states is slightly better than for our results with $\Sigma^{(\infty)}$. The reason for this is better treatment of the interaction between core and valence electrons. The 6s electrons were included in the initial Hartree-Fock procedure. Also, interaction between the 6p electron and the core is included in the CC approach in all-orders of the MBPT.

This doesn’t mean that the $V^{N-4}$ approximation is not good for lead. First, as can be seen from Table III inclusion of core-valence correlation does lead to systematic significant improvement of the accuracy and final results are very close to the experiment. Second, the fact that inclusion of the higher order core-valence correlations doesn’t always lead to improvement of energy intervals doesn’t mean that the $V^{N-3}$ approximation is not good. It rather means that not all dominating higher-order diagrams are included into $\Sigma^{(\infty)}$. The situation is very similar to what takes place for single-valence-electron atoms. The technique developed by us for alkali atoms [10] doesn’t work very well for atoms like thallium where interaction between valence electron and the core is important. Here CC+MBPT approach gives better results [12] which may mean that the combination of the CC approach with the CI method is a better option for atoms like lead. This approach was recently considered by Kozlov [16] and Johnson [17]. However, no calculations for real atoms have been done so far.

III. CONCLUSION

It has been demonstrated that the $V^{N-4}$ approximation works very well for the four-valence-electrons atoms like germanium, tin and lead as well as for their single, double and triple ionized ions. The use of the $V^{N-4}$ approximation makes it easy to include core-valence correlations beyond the second order of the MBPT. Inclusion of the core-valence correlations leads to significant improvement of the results in all cases. In general, the $V^{N-M}$ approximation (M is the number of valence electrons) is a good approximation if the overlap between core and valence states is small. The best case is the alkaline-earth atoms where the $V^{N-2}$ approximation must produce excellent results. In contrast, the $V^{N-M}$ approximation is not applicable at all to atoms with open d or/and f shells unless uppermost core s and p states are also treated as valence states. It should work more or less well for most of the atoms/ions with s and/or p valence electrons. In cases of relatively large overlap between core and valence states good results can still be achieved if accurate treatment of the interaction between core and valence electron is included perturbatively into the calculation of the core-valence correlations.

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| State  | CI      | $\Sigma^{(2)}$ | $\Sigma^{(\infty)}$ | $f\Sigma^{(\infty)}$ | Ref. [15] | Exp. [14] |
|--------|---------|----------------|---------------------|-----------------------|-----------|-----------|
|        | Pb IV   |                |                     |                       |           |           |
| $5d^{10}6s$ | $^2S_{1/2}$ | RE -1.48374 | -1.57689 | -1.56035 | -1.55529 | -1.55531 |
| $5d^{10}6p$ | $^2P_{1/2}$ | 72857 | 78055 | 78239 | 76144 | 76158 |
|        | $^2P_{3/2}$ | 92031 | 99817 | 99388 | 97276 | 97219 |
| $5d^{10}6d$ | $^2D_{3/2}$ | 173446 | 188501 | 185992 | 184570 | 184559 |
|        | $^2D_{5/2}$ | 175485 | 190789 | 188254 | 186848 | 186817 |
|        | Pb III   |                |                     |                       |           |           |
| $6s^2$ | $^1S_0$  | RE -2.58923 | -2.76503 | -2.73356 | -2.72421 | -2.72853 |
| $6s6p$ | $^3P_0$  | 52866 | 62881 | 62947 | 61045 | 60397 |
|        | $^3P_1$  | 57184 | 66767 | 66751 | 64851 | 64391 |
|        | $^3P_2$  | 70223 | 82032 | 81477 | 79577 | 78985 |
|        | $^1P_1$  | 91945 | 96556 | 95876 | 94071 | 95340 |
| $6p^2$ | $^3P_0$  | 135286 | 145385 | 145400 | 141555 | 142551 |
| $6s7s$ | $^1S_1$  | 137664 | 153445 | 150863 | 150038 | 150084 |
| $6s6d$ | $^1D_2$  | 138279 | 156137 | 154498 | 152079 | 151885 |
| $6s7s$ | $^1S_0$  | 142139 | 156815 | 154219 | 153407 | 153783 |
| $6s^26p$ | $^2P_{1/2}^{o}$ | RE -3.11363 | -3.31759 | -3.27430 | -3.26897 | -3.28141 |
| $6s^26d$ | $^2P_{3/2}^{o}$ | 12300 | 14447 | 13858 | 13896 | 14137 | 14081 |
| $6s6p^2$ | $^4P_{1/2}$ | 50298 | 59934 | 59934 | 58052 | 57911 |
|        | $^4P_{3/2}$ | 57290 | 68501 | 67633 | 66221 | 66124 |
|        | $^4P_{5/2}$ | 61484 | 75957 | 74856 | 73479 | 73905 |
| $6s^27s$ | $^2S_{1/2}$ | 55451 | 60525 | 58170 | 59203 | 58967 | 59448 |
| $6s^26d$ | $^2D_{5/2}$ | 66823 | 71130 | 69314 | 69256 | 70229 | 68964 |
|        | $^2D_{3/2}$ | 63732 | 70711 | 68916 | 69001 | 69688 | 69740 |
| $6s^27p$ | $^2P_{3/2}^{o}$ | 69961 | 75342 | 73140 | 73878 | 74256 | 74549 |
|        | $^2P_{1/2}^{o}$ | 72572 | 78180 | 75935 | 76666 | 77069 | 77272 |
| $6s6p^2$ | $^2D_{3/2}$ | 77272 | 85538 | 84523 | 83196 | 83083 | 83072 |
|        | $^2D_{5/2}$ | 81630 | 91291 | 89614 | 88800 | 88972 |
| Pb II  |                |                     |                       |                       |           |           |
| $6s^26p^2$ | $^3P_0$ | RE -3.36433 | -3.58255 | -3.53174 | -3.52974 | -3.55398 | 7819 |
| $^3P_1$ | 6388 | 7736 | 7395 | 7335 | 7559 |
| $^3P_2$ | 9199 | 10795 | 10277 | 10423 | 10650 |
| $^3D_2$ | 18578 | 21793 | 20780 | 20979 | 21458 |
| $^1S_0$ | 26998 | 30355 | 29185 | 29412 | 29467 |
| $6s^26p7p$ | $^3P_0$ | 33413 | 35239 | 33679 | 34517 | 34960 |
| $^3P_1$ | 33871 | 35610 | 34056 | 34887 | 35287 |
| $^3P_2$ | 40029 | 42987 | 41405 | 42061 | 42919 |
| $^3P_0$ | 41612 | 44441 | 42882 | 43525 | 44401 |
| $6s^26p7p$ | $^2D_1$ | 41740 | 44714 | 43129 | 43773 | 44675 |
| $^2D_2$ | 41886 | 44868 | 43281 | 43958 | 44809 |