

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

V. A. Dzuba\*

*School of Physics, University of New South Wales, Sydney 2052, Australia*

(Received 18 February 2005; published 1 June 2005)

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 previous work [Dzuba, Phys. Rev. A **71**, 032512 (2005)] [ $M$  is the number of valence electrons ( $M=4$ )]. 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 leads to systematic improvement of the accuracy of calculations for all ions and neutral atoms.

DOI: 10.1103/PhysRevA.71.062501

PACS number(s): 31.25.Eb, 31.25.Jf

## 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 [2] 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

$$\omega = \omega_0 + qx, \quad (1)$$

where  $x=(\alpha/\alpha_0)^2-1$  and  $\alpha_0$  and  $\omega_0$  are the current 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  $1/\nu^3$  [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 pseudocrossing calculation of  $q$  coefficients may become very unstable [4]. In the vicinity of level pseudocrossing 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 pseudocrossing always means strong configuration mixing between the states. However, strong configuration

mixing may also take place without level pseudocrossing. This can also cause instability in calculated values of  $q$  coefficients. Indeed, relativistic correction to the energy of a single electron state  $|n_j l m\rangle$  strongly depends on the total momentum  $j$  of this state (see, e.g., formula (7) in Ref. [3]). Therefore configurations composed from states of different  $j$  may have very different values of  $q$  and small error in the configuration mixing coefficients would lead to large error in the resulting  $q$  value for the mixed state [5].

Strong configuration mixing and level pseudocrossing take place for Ge II, Sn II, and Pb II ions [2] as well as for many other atoms and ions [4]. 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., [6]), atomic clocks [7], interaction of positrons with atoms [8], 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 does not matter which core states are used to calculate the potential-states of the neutral atom or states of the closed-shell positive ion.

The effective Hamiltonian for valence electrons is constructed using the configuration interaction (CI) technique. Core-valence correlations are included by adding the elec-

\*Electronic address: v.dzuba@unsw.edu.au

tron correlation operator  $\hat{\Sigma}$  to the CI Hamiltonian. Many-body perturbation theory (MBPT) is used to calculate  $\hat{\Sigma}$ . The main advantage of the  $V^{N-M}$  approximation is that MBPT is relatively simple (no subtraction diagrams) and the  $\hat{\Sigma}$  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 previous work [1] the  $V^{N-M}$  approximation was used for Kr and Ba while higher-order core-valence correlations were included for Ba and Ba<sup>+</sup> only. In the present work we study 12 complicated many-electron systems including germanium, tin, lead, and their positive ions. We demonstrate that using the  $V^{N-4}$  approximation ( $M=4$  for the case of Ge, Sn, and Pb) and accurate treatment of the core-valence correlations leads to high accuracy of calculations for all 12 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

$$\hat{H}^{\text{eff}} = \sum_{i=1}^M \hat{h}_{1i} + \sum_{i \neq j}^M \hat{h}_{2ij}, \quad (2)$$

$\hat{h}_1(r_i)$  is the one-electron part of the Hamiltonian

$$\hat{h}_1 = c\alpha \cdot \mathbf{p} + (\beta - 1)mc^2 - \frac{Ze^2}{r} + V^{N-4} + \hat{\Sigma}_1. \quad (3)$$

$\hat{\Sigma}_1$  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., [9]). It can be calculated in the second-order of the MBPT. Selected chains of the higher-order diagrams can be included into  $\hat{\Sigma}_1$  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

$$\hat{h}_2 = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \hat{\Sigma}_2(r_1, r_2), \quad (4)$$

$\hat{\Sigma}_2$  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  $\hat{\Sigma}_1$  is more important than for  $\hat{\Sigma}_2$ . The details of the calculation of  $\hat{\Sigma}_1$  and  $\hat{\Sigma}_2$  can be found elsewhere [9–12]. 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  $V^{N-4}$ ,  $\hat{\Sigma}_1$  and  $\hat{\Sigma}_2$  remain exactly the same.

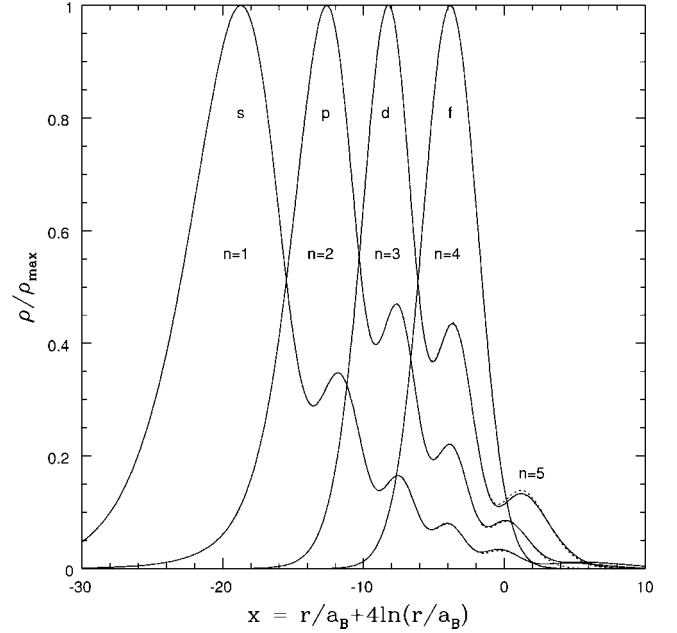


FIG. 1. Electron density of the  $s$ ,  $p$ ,  $d$ , and  $f$  electrons of Pb I and Pb V.

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  $\hat{\Sigma}$  operator would have terms proportional to  $V^{N-4} - V$  (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 82 electrons occupying six shells. Angular momentum  $l$  ranges from 0 ( $s$  electrons) to 3 ( $f$  electrons). Figures 1 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:

$$\rho(r)_l = \sum_{njm} |\psi(r)_{njlm}|^2 r^2.$$

The values of  $\rho(r)_l$  in the maximum are very different for different  $l$ . Therefore, we present normalized functions  $\rho(r)_l / \rho_{\text{max}}$  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  $n-l=1, 2$ , 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 in Fig. 1. Figure 2 presents details of the right bottom corner of

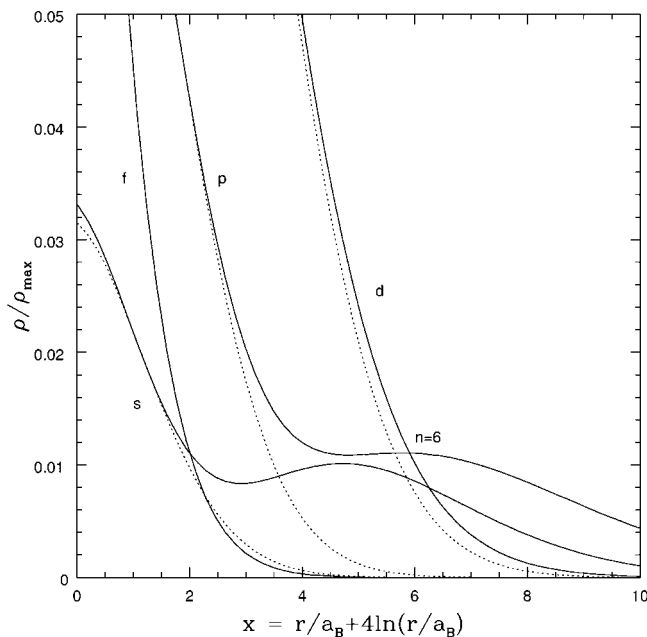


FIG. 2. Details of electron densities of Pb I and Pb V at large distances.

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 at shorter distances. This is because valence electrons are localized at 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.

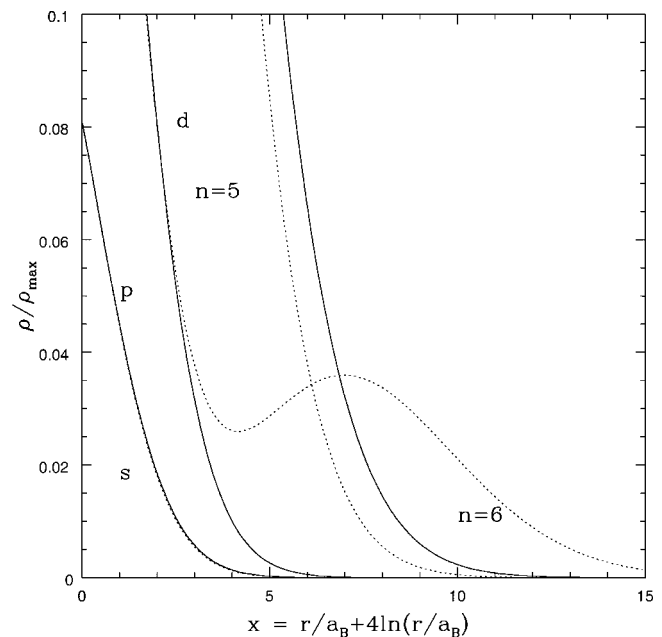


FIG. 3. Electron densities of Ba I and Ba III at large distances.

### B. Calculations for germanium

Germanium is the lightest of three atoms ( $Z=32$ ) and the easiest from a 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 the small number of electrons in the core.

We calculate  $\hat{\Sigma}_1$  and  $\hat{\Sigma}_2$  for the effective Hamiltonian (2) in the second order of the MBPT. Inclusion of  $\hat{\Sigma}_1$  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] does not 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  $\text{cm}^{-1}$ . Column marked CI presents the results of the standard configuration interaction method without  $\hat{\Sigma}$ . Column  $\hat{\Sigma}^{(2)}$  presents the results of calculations with the effective Hamiltonian (2) in which  $\hat{\Sigma}$  is calculated in the second order of MBPT.

The results presented in Table I show that inclusion of the core-valence correlations leads to systematic significant im-

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

State		CI	$\hat{\Sigma}^{(2)}$	Expt. [13]	
Ge IV					
$4s_{1/2}$	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	
$4d_{3/2}$		184049	191424	190861	
Ge III					
$4s^2$	$1S_0$	RE	-2.85213	-2.93114	-2.93765
$4s4p$	$3P_0$		57762	61812	61734
	$3P_1$		58490	62595	62500
	$3P_2$		60030	64273	64144
$4s4p$	$1P_1$		90820	92238	91873
$4s4d$	$1D_2$		137686	145305	144975
$4p^2$	$3P_0$		142850	148023	147685
	$3P_1$		143721	148997	148640
	$3P_2$		145276	150765	150372
$4s5s$	$3S_1$		152184	158630	158565
Ge II					
$4s^24p$	$2P_{1/2}^o$	RE	-3.42509	-3.51488	-3.52322
	$2P_{3/2}^o$		1623	1797	1767
$4s4p^2$	$4P_{1/2}$		47667	51512	51576
	$4P_{3/2}$		48326	52241	52291
	$4P_{5/2}$		49333	53342	53367
$4s^25s$	$2S_{1/2}$		61124	62870	62402
$4s4p^2$	$2D_{3/2}$		61750	65313	65015
	$2D_{5/2}$		61930	65494	65184
$4s^25p$	$2P_{1/2}^o$		77370	79386	79006
	$2P_{3/2}^o$		77710	79750	79366
$4s^24d$	$2D_{3/2}$		79270	81444	80836
	$2D_{5/2}$		79439	81625	81012
Ge I					
$4s^24p^2$	$3P_0$	RE	-3.70376	-3.79871	-3.81352
	$3P_1$		493	556	557
	$3P_2$		1276	1423	1410
$4s^24p^2$	$1D_2$		7320	7591	7125
$4s^24p^2$	$1S_0$		17093	17541	16367
$4s^24p5s$	$3P_0$		38969	38665	37452
	$3P_1$		39272	38963	37702
	$3P_2$		39024	40385	39118
$4s^24p5s$	$1P_1$		42010	41648	40020
$4s^24p5p$	$1P_1$		45489	45503	45985
$4s^24p5p$	$3D_1$		46246	46199	46765
	$3D_2$		46332	46275	46834
	$3D_3$		47469	47620	48104

provement 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  $\dots 5s^25p^2$ . 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  $\hat{\Sigma}_1$ . It is done exactly the same way as in our calculations for single-valence-electron atoms (see, e.g., [10]). The  $\hat{\Sigma}_2$  operator is still calculated in the second order of the MBPT.

The results are presented in Table II. There is one more column in the table compared to Table I. It is marked  $\hat{\Sigma}_1^{(\infty)}$  and presents the results of calculations with all-order  $\hat{\Sigma}_1$ . Again, it is easy to see that moving from less sophisticated to more sophisticated approximations (with no  $\hat{\Sigma}_2$ ; with  $\hat{\Sigma}_2^{(2)}$ ; with  $\hat{\Sigma}_2^{(\infty)}$ ) 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 nonrelativistic 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 factors before  $\hat{\Sigma}_1$  to fit the energies of Pb IV. These energies are found by solving Hartree-Fock-like equations for the states of external electron of Pb IV in the  $V^{N-4}$  potential of the atomic core

$$(\hat{H}_0 + \hat{\Sigma}_1 - \epsilon_n)\psi_n = 0. \quad (5)$$

Here  $\hat{H}_0$  is the Hartree-Fock Hamiltonian.  $\hat{\Sigma}_1$  is the all-order correlation potential operator similar to what is used for tin. Inclusion of  $\hat{\Sigma}_1$  takes into account the effect of the core-valence correlations on both the energies ( $\epsilon_n$ ) and the wave functions ( $\psi_n$ ) of the valence states producing the so-called Brueckner orbitals. The difference between Brueckner and experimental energies of the  $4s$ ,  $4p$ , and  $4d$  states of Pb IV are on the level of 0.2%–0.4% (for removal energies). To further improve the energies we replace  $\hat{\Sigma}_1$  by  $f\hat{\Sigma}_1$  with rescaling factor  $f$  chosen to fit the energies exactly. Then the same rescaled operator  $f\hat{\Sigma}_1$  is used for the Pb III and Pb II ions and for the Pb I. It turns out that only small rescaling is needed. Maximum deviation of the rescaling factor from

TABLE II. Ground state removal energies (RE, a.u.) and excitation energies (cm<sup>-1</sup>) of low states of Sn IV to Sn I.

State	CI	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	Expt. [14]	
Sn IV					
$4d^{10}5s$	$^2S_{1/2}$ RE	-1.43894	-1.51228	-1.49776	-1.49699
$4d^{10}5p$	$^2P_{1/2}$	66323	70709	69727	69564
	$^2P_{3/2}$	72291	77409	76264	76072
$4d^{10}5d$	$^2D_{3/2}$	156481	168074	165406	165305
	$^2D_{5/2}$	157180	168847	166183	165411
Sn III					
$5s^2$	$^1S_0$ RE	-2.51142	-2.64097	-2.61447	-2.61794
$5s5p$	$^3P_0^o$	47961	54914	54001	53548
	$^3P_1^o$	49548	56582	55631	55196
	$^3P_2^o$	53207	60734	59670	59229
	$^1P_1^o$	78801	80163	79019	79911
$5p^2$	$^3P_0$	121290	128814	126873	127309
	$^3P_1$	123690	131743	129709	130120
	$^3P_2$	118412	136470	134275	134567
	$^1D_2$	127379	130638	128478	128205
$5s6s$	$^3S_1$	130986	141420	139341	139638
$5s5d$	$^3D_1$	132760	142898	140463	141322
	$^3D_2$	132946	143107	140671	141526
	$^3D_3$	133222	143423	140987	141838
$5s6s$	$^1S_0$	135453	145105	143064	143591
$5s5d$	$^1D_2$	148378	155394	153063	154116
Sn II					
$5s^25p$	$^2P_{1/2}^o$ RE	-3.03218	-3.17791	-3.14624	-3.15567
	$^2P_{3/2}^o$	3776	4352	4222	4251
$5s5p^2$	$^4P_{1/2}$	40839	47579	46661	46464
	$^4P_{3/2}$	42512	49537	48556	48368
	$^4P_{5/2}$	44720	51958	50915	50730
$5s^26s$	$^2S_{1/2}$	54896	57545	56707	56886
$5s5p^2$	$^2D_{3/2}$	54142	59969	58806	58844
	$^2D_{5/2}$	54731	60599	59419	59463
$5s^25d$	$^2D_{3/2}$	69220	72247	71140	71406
	$^2D_{5/2}$	69776	72929	71804	72048
$5s^26p$	$^2P_{1/2}^o$	69006	72131	71182	71494
	$^2P_{3/2}^o$	69825	73025	72061	72377
Sn I					
$5s^25p^2$	$^3P_0$ RE	-3.28899	-3.44213	-3.407850	-3.425548
	$^3P_1$	1411	1681	1623	1692
	$^3P_2$	3049	3539	3428	3428
	$^1D_2$	8359	9079	8891	8613
	$^1S_0$	17328	18217	17977	17163
$5s^25p6s$	$^3P_0$	35381	35722	35251	34641
	$^3P_1$	35764	36050	35577	34914
	$^3P_2$	38988	39848	39252	38629
	$^1P_1$	40080	40655	40063	39257
$5s5p^3$	$^5S_2$	34720	40529	39725	39626

TABLE II. (Continued.)

State	CI	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	Expt. [14]	
$5s^25p6p$	$^3P_0$	42805	44164	43578	43430
	$^3P_1$	41361	42785	42200	42342
	$^3P_2$	45804	47712	47008	47235
$5s^25p6p$	$^3D_1$	42356	43768	43178	43369
	$^3D_2$	42447	43861	43267	43239
	$^3D_3$	45543	47511	46796	47007

unity is 10%:  $f(4s)=0.935$ ,  $f(4p_{1/2})=1.084$ ,  $f(4p_{3/2})=1.1$ ,  $f(4d_{3/2})=1.07$ ,  $f(4d_{5/2})=1.07$ .

The results of the calculations are presented in Table III. Again, inclusion of core-valence correlations lead to significant improvement of the accuracy of the results in all cases. However, comparison between different ways of treating core-valence correlations reveal a more complicated situation compared to what we have for tin. When we move from the second-order correlation operator  $\hat{\Sigma}^{(2)}$  to the all-order  $\hat{\Sigma}^{(\infty)}$  and then to the rescaled  $f\hat{\Sigma}^{(\infty)}$  the improvement in accuracy is apparent for the removal energies. It is again systematic and significant, bringing results for all states of all ions and neutral lead to better agreement with experiment. This is not always the case for the energy intervals. When a more accurate treatment of core-valence correlation is introduced two energy levels may move towards experimental values at a slightly different rate so that the interval between them does not improve. In Table III we present removal energies only for the ground states of Pb IV, Pb III, Pb II, and Pb I. Energies of excited states are given with respect to the ground state. It is easy to see that energy intervals between ground and excited states calculated with second-order  $\hat{\Sigma}$  are often in better agreement with experiment than the results with the all-order  $\hat{\Sigma}$ . In general, the results are not as good as for tin. The reason for this is a larger overlap between valence and core states. Relativistic effects cause stronger binding of the  $6s$  and  $6p$  electrons of Pb compared to binding of the  $5s$  and  $5p$  electrons of Sn. This means that overlap between valence and core states is also larger for lead than for tin, leading to larger effect of removal of valence electrons on atomic core.

It is instructive to compare our results with the results of 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  $\hat{\Sigma}^{(\infty)}$ . 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 does not mean that the  $V^{N-4}$  approximation is not good for lead. First, as can be seen from Table III, inclusion

TABLE III. Ground state removal energies (RE, a.u.) and excitation energies (cm<sup>-1</sup>) of low states of Pb IV to Pb I.

State		CI	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	$f\hat{\Sigma}^{(\infty)}$	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
	$^2P_{3/2}$	92301	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
$6s7s$	$^3S_1$	137664	153445	150863	150038		150084
$6s6d$	$^1D_2$	138279	156137	154498	152079		151885
$6s7s$	$^1S_0$	142139	156815	154219	153407		153783
Pb II							
$6s^26p$	$^2P_{1/2}^o$ RE	-3.11363	-3.31759	-3.27430	-3.26897		-3.28141
	$^2P_{3/2}^o$	12390	14447	13858	13896	14137	14081
$6s6p^2$	$^4P_{1/2}$	50298	59934	59934	58052		57911
	$^4P_{3/2}$	57209	68501	67633	66221		66124
	$^4P_{5/2}$	61484	75957	74856	73749		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	69686	69740
$6s^27p$	$^2P_{1/2}^o$	69961	75342	73140	73878	74256	74459
	$^2P_{3/2}^o$	72572	78180	75935	76666	77069	77272
$6s6p^2$	$^2D_{3/2}$	77272	85538	84523	83196		83083
	$^2D_{5/2}$	81630	91291	89614	88800		88972
Pb I							
$6s^26p^2$	$^3P_0$ RE	-3.36433	-3.58255	-3.53174	-3.52974		-3.55398
	$^3P_1$	6388	7736	7305	7353		7819
	$^3P_2$	9199	10795	10277	10423		10650
	$^1D_2$	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
$6s^26p7p$	$^3P_1$	40029	42987	41405	42061		42919
	$^3P_0$	41612	44441	42882	43525		44401
$6s^26p7p$	$^3D_1$	41740	44714	43129	43773		44675
	$^3D_2$	41886	44868	43281	43958		44809

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 does not always lead to improvement of energy intervals does not mean that the

$V^{N-4}$  approximation is not good. It rather means that not all dominating higher-order diagrams are included into  $\hat{\Sigma}^{(\infty)}$ . The situation is very similar to what takes place for single-valence-electron atoms. The technique developed by us for

alkali atoms [10] does not work very well for atoms like thallium where interaction between valence electron and the core is important. Here the CC+MBPT approach gives better results [15] 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.

### III. CONCLUSION

It has been demonstrated that the  $V^{N-4}$  approximation works very well for the four-valence-electron atoms, such as 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 and/or 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 electrons is included perturbatively into the calculation of the core-valence correlations.

### ACKNOWLEDGMENTS

The author is grateful to J. S. M. Ginges and V. V. Flambaum for useful discussions.

- 
- [1] V. A. Dzuba, Phys. Rev. A **71**, 032512 (2005).
  - [2] V. A. Dzuba and V. V. Flambaum, e-print physics/0501454; Phys. Rev. A (to be published).
  - [3] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. A **59**, 230 (1999).
  - [4] V. A. Dzuba, V. V. Flambaum, M. G. Kozlov, and M. Marchenko, Phys. Rev. A **66**, 022501 (2002).
  - [5] Strictly speaking, different values of  $q$  for different configurations would unavoidably lead to level crossing because  $q$  is a slope of the  $E(\alpha^2)$  graph. When we say "there is no level crossing" we mean that level crossing takes place far away from  $\alpha=\alpha_0$ .
  - [6] J. S. M. Ginges and V. V. Flambaum, Phys. Rep. **397**, 63 (2004).
  - [7] E. J. Angstmann, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A **70**, 014102 (2002).
  - [8] G. F. Gribakin and J. Ludlow, Phys. Rev. A **70**, 062717 (2004).
  - [9] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B **20**, 3297 (1987).
  - [10] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, Phys. Lett. A **140**, 493 (1989).
  - [11] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).
  - [12] V. A. Dzuba and W. R. Johnson, Phys. Rev. A **57**, 2459 (1998).
  - [13] NIST Atomic Spectra Database on Internet, [http://physics.nist.gov/cgi-bin/AtData/main\\_asd](http://physics.nist.gov/cgi-bin/AtData/main_asd).
  - [14] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.), Circ. No. 467 (U.S. GPO, Washington, D.C., 1958), Vols. 1–3.
  - [15] U. I. Safronova, M. S. Safronova, and W. R. Johnson, e-print physics/0410079; Phys. Rev. A (to be published).
  - [16] M. G. Kozlov, Opt. Spectrosc. **95**, 6 (2003); Int. J. Quantum Chem. **100**, 336 (2004).
  - [17] W. R. Johnson (unpublished).