Many-body perturbation-theory calculations in atoms with open shells

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Energy intervals, g factors, and $M1$ amplitudes of the $6p^2$ configuration in Pb and the $6p^3$ configuration in Bi are calculated. All the corrections of second-order perturbation theory in residual electron-electron interaction are taken into account. The higher-order corrections are also investigated. In Pb we have calculated the most important corrections: the screening of external electrons interaction by closed-shell polarization. In Bi the higher-order corrections are treated semiempirically. Energy levels for a superheavy element with charge $Z=114$ are also calculated.

In the past few years, methods [1–5] have been developed that allow us to calculate with high accuracy the energy levels and other spectroscopic characteristics of heavy atoms with one external electron above the closed shells with high accuracy. These high-precision atomic calculations were stimulated by the interest in reliable prediction for parity-nonconservation effects in heavy atoms (see, e.g., Ref. [6] and references therein). The following and much more complicated problems are the investigation of atoms with few external electrons.

In the present work the technique developed in Refs. [1], [3], and [5] was applied to the investigation of Pb and Bi atoms. The energy intervals and g factors of $6p^2$ and $6p^3$ configurations were calculated. We have also calculated the amplitudes of $M1$ transitions. These amplitudes are necessary to obtain useful information from the parity-violation experiments on Pb and Bi (see, e.g., Ref. [7]). Note that preliminary results of the present work (configuration wave functions and $M1$ amplitudes) were used by us in the calculation of parity nonconservation in Pb and Bi atoms [8].

Unlike the external electron ionization energy, the energy intervals and structure of configurations in Pb and Bi are determined mostly by the residual electron-electron interaction, which we treat by means of perturbation theory. This is the reason for the accurate account of correlation corrections. All the corrections of the second-order perturbation theory in the residual interaction were calculated. The higher-order corrections were taken into account by different methods for Pb and Bi. The most important higher-order corrections correspond to collective screening of electron-electron interactions [3]. In Pb the screening of electron-electron interaction due to closed-shell polarization was calculated. In Bi the higher-order effects were treated semiempirically. Practically, only two fitting parameters are needed for accurate description of energy intervals, g factors, and $M1$ amplitudes inside the $6p^3$ configuration.

We use the relativistic Hartree-Fock method as a zero approximation. The exact Hamiltonian of an atom is divided into two parts. The first part is a sum of single-particle Hamiltonians allowing an exact numerical solution, and the second part represents the remaining ("residual") interaction which can be taken into account in terms of perturbation theory:

$$H=\sum_i H_0(r_i)+U \tag{1}$$

where

$$H_0=c\underline{\alpha}\mathbf{p}+(\underline{\beta}-1)mc^2-\frac{Ze^2}{r}+V\ . \tag{2}$$

Here $\underline{\alpha}$ and $\underline{\beta}$ are Dirac matrices, Z is the nucleus charge,

$$U=\sum_{i<j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}-\sum_i V(r_i)\ . \tag{3}$$

The single-particle potential V has the form

$$V=V_{\mathrm{HF}}+V_{6p}\ . \tag{4}$$

Here V_{HF} is the Hartree-Fock potential of closed shells (both direct and exchange). V_{6p} in Pb is the angular-independent part (zero harmonic) of one external $6p$ electron potential and in Bi it is the angular-independent part of the potential of two $6p$ electrons (V^{N-1} approximation). The Hartree-Fock potential V_{HF} added to (3) leads to the exact cancellation of a certain class of diagrams, namely those diagrams which describe an interaction with closed-shell electrons without their excitation. Similar to V_{HF}, the field of external shell V_{6p} is canceled out in perturbation theory diagrams. But this cancellation is approximate only, because of the difference of $6p_{1/2}$ and

$6p_{3/2}$ electron electric fields.

In atoms that have one external electron there are now first-order corrections to ionization energy because of adequate choice of zero approximation. In Pb and Bi there are two reasons which lead to $6p^n$ configuration splitting. The first effect, which appears already in the first order of perturbation theory, is the interaction of external $6p$ electrons. The second effect is the $6p$-level fine structure. This is a simple single-particle effect.

The second-order corrections to the mixing of configurations and energy-level splitting are shown in Fig. 1. We use the Feynman perturbation theory technique for drawing these diagrams. In this technique the number of diagrams is essentially smaller than in the usual Brueckner-Goldstone many-body perturbation theory technique. Moreover, the Feynman technique allows us to calculate in Pb an infinite chain of diagrams corresponding to collective screening of Coulomb interaction by closed-shell polarization [3,5].

The details of the Feynman-diagram calculations (Green function in Hartree-Fock field, polarization operator, integration over frequencies, diagram summation) are described in Refs. [3] and [5]. The diagrams, Fig. 1(a), are the renormalization of the external-electron interaction. Most important here is the first diagram, (i) which is the only one without closed-shell electron excitation. The Fig. 1(b) diagrams change the single-particle energy. These diagrams give corrections to $6p$ level fine structure which we calculate quite accurately. In Fig. 1(c), we have shown the diagram describing the interaction of three $6p$ electrons which appear in Bi only.

Energy levels, g factors, and $M1$ amplitudes of the $6p^2$ Pb and $6p^3$ Bi configurations calculated in first and second orders of perturbation theory are shown in Tables I–III. Due to relatively small energy intervals, the matrix of interaction between the $6p^2$ (or $6p^3$) configuration components was diagonalized exactly. We see that the first-order correction is comparable with fine-structure splitting, and the second-order correction is only two times smaller than the first one.

As was shown in Refs. [3–5] for the Tl and Cs atoms, there are two of the most important effects among the higher-order corrections (Fig. 2). The first effect [Fig. 2(a)] is a strong collective screening of the external electrons interaction by the closed-shell polarization. The second [Fig. 2(b)] is an attraction of particles and holes in closed shells which reduces effectively the energy denominators in perturbation theory graphs. In atoms with one unpaired electron these two effects strongly cancel each other, which is a source of reasonable accuracy for the

TABLE I. Energy levels and g factors of the Pb $6p^2$ configuration.

	a	b	c	d	Expt.
			Energy levels (cm^{-1})		
$^3P'_0$	0	0	0	0	0
$^3P_1$	10 303	6 779	8 692	8 165	7 819[e]
$^3P'_2$	10 303	10 414	10 838	10 504	10 651[e]
$^1D'_2$	20 606	21 571	21 691	21 326	21 458[e]
$^1S'_0$	20 606	31 807	28 258	29 729	29 467[e]
			g factors (cm^{-1})		
$^3P'_2$	1.167	1.315	1.248	1.246	1.2753(4)[f]
$^1D'_2$	1.333	1.185	1.252	1.254	1.2263(1)[g]

[a]Zero order over residual electron-electron interaction.
[b]First order.
[c]Second-order calculations.
[d]Second order over residual interaction plus screening of external-electron interaction by the closed-shell polarization.
[e]Reference [10].
[f]Reference [11].
[g]Reference [12].

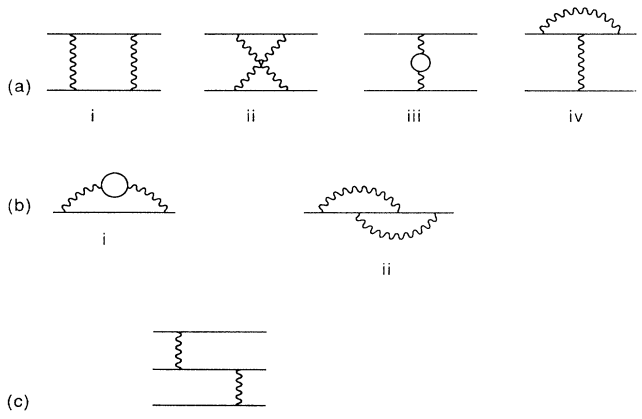

FIG. 1. The second-order electron-electron interaction diagrams: (a) the two external-electron interaction, (b) the single-particle energy correction, (c) the three external-electron interaction which appears in the Bi $6p^3$ configuration only. The external lines in diagrams correspond to $6p$ electron states. We have not shown here diagrams with single-particle operator V_{6p} [Eq. (4)].

TABLE II. Energy levels and g factors of the Bi $6p^3$ configuration.

	a	b	c	Expt.
		Energy levels (cm^{-1})		
$^4S'_{3/2}$	0	0	0	0
$^2D'_{3/2}$	12 142	11 507	11 672	11 419[d]
$^2D_{5/2}$	16 793	15 320	15 593	15 438[d]
$^2P_{1/2}$	24 248	20 688	21 806	21 661[d]
$^2P'_{3/2}$	35 435	32 839	33 337	33 165[d]
		g factors (cm^{-1})		
$^4S'_{3/2}$	1.7481	1.5907	1.6445	1.6433(2)[e]
$^2D'_{3/2}$	1.1332	1.2884	1.2321	
$^2P'_{3/2}$	1.2527	1.2645	1.2594	1.2608(1)[f]

[a,b]The first and second orders over residual interaction are taken into account.
[c]The result of semiempirical treatment of higher-order correction.
[d]Reference [10].
[e]Reference [13].
[f]Reference [14].

TABLE III. $M1$ amplitudes in Bi.

Transition	a	b
$^4S'_{3/2}$-$^2D'_{3/2}$	−1.747	−1.695(9)
$^4S'_{3/2}$-$^2D_{5/2}$	0.615	0.563(6)
$^4S'_{3/2}$-$^2P_{1/2}$	0.625	0.590(5)
$^4S'_{3/2}$-$^2P'_{3/2}$	0.166	0.199(5)

[a]Second-order perturbation-theory calculation.
[b]Second-order calculation plus higher-order corrections treated semiempirically.

second-order perturbation-theory calculations [1,2].

Unlike the alkali-metal atoms, in Pb and Bi the main contribution to the mixing of $6p^n$ configurations comes from the direct interaction of two external electrons without closed-shell excitation [diagram (i) in on Fig. 1(a)]. For the Pb atom we have taken into account screening of the Coulomb interaction by closed-shell polarization only in these second-order diagrams. In other words, we have calculated the chain shown on Fig. 3. The method of calculation of Coulomb interaction screening was described in Refs. [3] and [5]. Concerning the renormalization of second-order diagrams $a2$-$a4$ with excited core electrons (holes) we suppose that the particle-hole attraction cancels numerically the essential part of the screening of Coulomb interaction (see discussion above). Results of high-order calculations in Pb are shown in Table I, column d. One can see that higher-order corrections (screening and particle-hole attraction diagrams) essentially improve the accuracy of calculations of energy levels.

We have also calculated the value of $M1$ amplitude $^3P'_0$-$^3P_1$ in Pb which is interesting for the interpretation of parity-violation experiments

$$A_{M1}=-1.29(1)\frac{e\hbar}{2mc} . \tag{5}$$

The reduced $M1$ amplitude is defined as ($J'\neq J$)

$$A_{M1}(-1)^{J'-J_z}\begin{pmatrix} J' & 1 & J \\ -J_z & 0 & J_z \end{pmatrix}$$
$$=\frac{e\hbar}{2mc}\langle J',J_z|L_z+2S_z|J,J_z\rangle$$
$$=\frac{e\hbar}{2mc}\langle J',J_z|S_z|J,J_z\rangle . \tag{6}$$

For calculating g factors and $M1$ amplitudes we use the fact that the overlapping of $6p_{1/2}$ and $6p_{3/2}$ radial wave functions is 0.98 both in Pb and Bi, and also include the correction $\alpha/2\pi$ in the free-electron g factor.

In Bi the second-order perturbation theory calculations are almost the same as in Pb. Only one additional second-order diagram appears [Fig. 1(c)] which connects three external $6p$ electrons. To evaluate the high-order effects in Bi we use a semiempirical approach. Let us neglect all the relativistic corrections in high-order effects. In this case, the residual Coulomb interaction conserves L—the total angular momentum of an atom. Thus all the high-order corrections may be expressed in terms of three matrix elements U_0, U_1, U_2 corresponding to Bi $6p^3$ available in configuration values of $L=0,1,2$. Moreover, the mixing and splitting of $6p^3$ configurations depend on only two values, U_1-U_0 and U_2-U_0. We have chosen the fitting parameters (in cm^{-1})

$$U_1-U_0=2115 ,$$
$$U_2-U_0=1277 . \tag{7}$$

Experience with calculations for atoms with one electron above the closed shells shows that second-order perturbation-theory calculations usually overestimate the fine structure of single electron levels. In Tl, whose $6p$ electron properties look very similar to those of $6p$ electrons in Pb and Bi, the accuracy of the second-order calculation of fine structure was $\simeq 2\%$ [9]. Therefore we have also reduced the fine structure of $6p$ single-particle energies in Bi by 300 cm^{-1} (2%). The improved values of energy levels, g factors, and $M1$ amplitudes in Bi are shown in Table I, column c.

For possible applications we present here expansion coefficients for the configurations $6p^2$ in lead and $6p^3$ in bismuth in a jj scheme. They are obtained by diagonalization of an interaction matrix calculated in second order with semiempirical treatment of higher orders (see above). Note that we neglect here the admixtures of higher configurations (for lowest states their weight is about 2%).

For Pb, $J=0$,

$$|^3P'_0\rangle=0.9744|\tfrac{1}{2}\tfrac{1}{2}\rangle-0.2246|\tfrac{3}{2}\tfrac{3}{2}\rangle ,$$
$$|^1S'_0\rangle=0.2246|\tfrac{1}{2}\tfrac{1}{2}\rangle+0.9744|\tfrac{3}{2}\tfrac{3}{2}\rangle .$$

Coefficients for $J=2$ states are easily extracted from g-factor values.

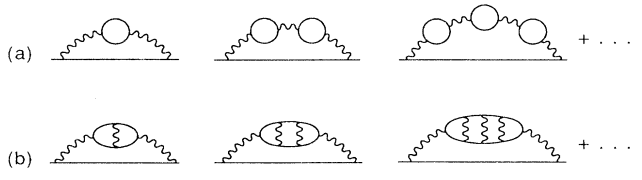

FIG. 2. The two most important chains of high-order diagrams in alkali-metal atoms: (a) the collective screening of the external-electron interactions, (b) the attraction of particles and holes in closed shells.

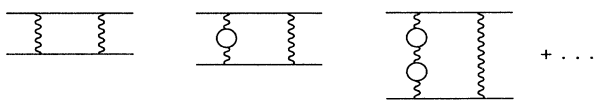

FIG. 3. The high-order diagrams which we have calculated in Pb.

TABLE IV. Energy levels (cm^{-1}) for Sn, Pb, and a superheavy element with $Z=114$. Zero corresponds to ion configuration $np_{1/2}$. Experimental values from Ref. [10].

		Sn		Pb		E114
		$n=5$ Calc.	$n'=6$ Expt.	$n=6$ Calc.	$n'=7$ Expt.	$n=7$, $n'=8$ Calc.
np^2	$^3P'_0$	−59 209	−59 232	−59 960	−59 821	−68 452
	$^3P_1$	−57 522	−57 540	−51 996	−52 002	−42 645
	$^3P'_2$	−55 786	−55 804	−49 174	−49 171	−40 061
	$^1D'_2$	−50 649	−50 619	−38 301	−38 363	−9 191
	$^1S'_0$	−42 099	−42 069	−30 282	−30 354	−3 934
$npn's$	$^3P_0$	−24 735	−24 591	−25 163	−24 861	−25 523
	$^3P_1$	−25 741	−24 318	−25 721	−24 534	−25 209

For Bi, $J=2$,

$$|^4S'_{3/2}\rangle = 0.9280\left|\tfrac{1}{2}\tfrac{1}{2}\tfrac{3}{2}\right\rangle - 0.3202\left|\tfrac{1}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle + 0.1904\left|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle ,$$

$$|^2D'_{3/2}\rangle = 0.3354\left|\tfrac{1}{2}\tfrac{1}{2}\tfrac{3}{2}\right\rangle + 0.9406\left|\tfrac{1}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle - 0.0526\left|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle ,$$

$$|^2P'_{3/2}\rangle = -0.1622\left|\tfrac{1}{2}\tfrac{1}{2}\tfrac{3}{2}\right\rangle + 0.1127\left|\tfrac{1}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle + 0.9803\left|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle .$$

The results for $M1$ amplitudes and expansion coefficients are in good agreement with semiempirical calculations [15]. As is known, there is an "island of stability" near a charge $Z=114$ nucleus. The corresponding atom $E114$ (configuration $7p^2$) is the analog of Sn ($5p^2$) and Pb ($6p^2$). It is interesting to calculate the spectrum of this atom. We obtained it using a direct calculation of first and second order for the interaction matrix of $7p^2$ states and extrapolation of higher orders for the np^2 configuration from a semiempirical fit in Sn and Pb (the method is similar to that we use for Bi). The results of a such calculation are presented in Table IV. For an estimation of the accuracy we present also the calculated and experimental energies for Sn and Pb.

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