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FINE- AND HYPERFINE STRUCTURE ANALYSIS OF THE ODD CONFIGURATIONS IN THE LEAD ATOM

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Abstract

The fine- and hyperfine structure (hfs) analysis, on the basis of available experimental data, for the configuration $6s^2 6p6d + 6s^2 6p7s + 6s^2 6p8s$ in PbI has been performed. The Slater integrals, spin-orbit parameters and the effective hfs one-electron parameters have been determined. We find an off-diagonal core-polarization effect in the 6p6d+6p7s - space. Using the calculated radial parameters, the values of the quadrupole moment for stable and radioactive Pb-nuclei have been determined from measured B-factors of the 6p7s $^3P_1$ state. In addition, a repulsion effect on the hfs sublevels with the same quantum number F has been investigated.

Fein- und Hyperfeinstruktur-Analyse der ungeraden Konfigurationen im Blei-Atom

Zusammenfassung

Es wurde eine Analyse der Fein- und Hyperfeinstruktur (Hfs) der beobachteten experimentellen Daten für die atomare Konfiguration $6s^2 6p6d + 6s^2 6p7s + 6s^2 6p8s$ in PbI durchgeführt. Slater-Integrale, Spin-Bahn-Parameter und effektive Hfs-Ein-Elektron-Parameter wurden bestimmt. Im 6p6d+6p7s-Raum finden wir einen off-diagonal-Rumpf-Polarisationseffekt. Aus den ermittelten Werten ergibt sich eine Relation zwischen gemessenen B-Faktoren des 6p7s $^3P_1$-Zustandes und nuklearen Quadrupolmomenten. Ein Abstoßungseffekt zwischen Hfs Zuständen zur gleichen Quantenzahl F wurde zusätzlich untersucht.

1. Introduction

There is a considerable interest in the nuclear structure information carried by hyperfine structure (hfs) splitting and isotope shifts of atomic transitions. Precise data on these effects allow to study electromagnetic moments of nuclei and the variation of nuclear charge radii in long isotopic chains, including nuclei far off stability. A typical example of this type of nuclear structure studies is provided by recent laser spectroscopic investigations [1] of the λ = 283.3 nm Pb I resonance line ($6p^2\ {}^3P_0$ - $6p7s\ {}^3P_1$) for a large number of stable and radioactive Pb isotopes. The interpretation of the directly observed quantities (hfs constants and isotopic line shifts) in terms of nuclear quantities requires a separation of nuclear and atomic structure effects. Usually, using some additional nuclear information, available for stable isotopes from other methods, the hfs and isotopic line shifts are calibrated in terms of nuclear moments and radii, since all ab initio calculations of the atomic structure ingredients are not able to provide sufficiently accurate results. Nevertheless a careful consideration of the atomic structure involved is necessary for controlling systematic uncertainties of the quoted values of the nuclear quantities.

In this paper and in context of the Pb studies above mentioned, we analyse the involved atomic configurations in a semi-empirical way, that means by introducing the empirical knowledge available about fine and hyperfine structure. In particular, the studies aim at

(i) a semi-empirical determination of possible contributions from atomic structure to the odd-even staggering observed for the Pb I resonance line (and, usually, totally ascribed to the variation of the charge radii).

(ii) the extraction of quadrupole moment values from the measured B-factors on the basis of the atomic structure knowledge.

In order to attack these questions, we consider simultaneously fine- and hyperfine structure. The fine structure analysis provides the intermediate-coupling eigenvector amplitudes which are a prerequisite for the determination of the hfs one-electron parameters.

2. Experimental data on atomic structure

The energy levels of PbI compiled in Ref. 2 are based on the analysis by Gieseler and Grotrian [3] with many additions and improvements resulting from the otherwise unpublished work of Meggers (1955). Measurements in the vacuum-UV absorption spectrum by Garton and Wilson [4] and by Brown et al. [5] have extended the number of known odd levels. Wood and Andrew [6,7] reinvestigated the Pb I emission spectrum and improved the values of wavelength and energy of a total of 59 even and 58 odd parity levels. However, in spite of this impressive amount of data, there remains missing information, even for low-lying odd configurations, under consideration in this paper. In addition, some results reported in Refs. 2,4,5 and 8 on the energy levels of the $6s^2 6p6d$ and $6s^2 6p8s$ are contradictory. Due to this situation there are some difficulties and complications when constructing the eigenvectors.

By the laser spectroscopic measurements of the PbI resonance line, the hfs of the $^3P_1$ level (originating, dominantly from the $6s^2 6p7s$ configuration) is precisely measured, not only for the stable odd nuclide. It has been observed [7] that in lead the odd configurations interact with each other rather strongly due to the Coulomb interaction, so that mixing of the configurations $6s^2 6p7s + 6s^2 6p6d + 6s^2 6p8s$ has to be expected. The hyperfine structure of some levels in these configurations has been recently measured by atomic beam laser spectroscopy [9] extending earlier measurements of Murakawa [10] and Blaise [11]. For ^{207}Pb the hfs splittings of eight levels ascribed to the $6p7s+6p6d+6p8s$ configurations are experimentally known and at disposal for a determination of the hfs one-electron radial parameters in the lead atom.

3. Fine structure analysis

Our aim is to order the fine structure levels of the triplet terms and to construct the eigenvectors of the $6s^2 6p7s$ + $6s^2 6p6d$ + $6s^2 6p8s$ configuration based on the Hamiltonian [12]

$$H = H_{el} + H_{magn} = \sum_{j>i} \frac{e^2}{r_{ij}} + \sum_i \xi_i(\vec{r}_i)\ (\vec{s}_i \cdot \vec{l}_i) \qquad (3.1)$$

The sums are carried out over all electrons of non closed shells. Less important terms concerning the orbit-orbit, spin-spin and spin-other-orbit magnetic interactions have been omitted in (3.1).

The electrostatic part of (3.1) is easily evaluated in the SL representation where the matrix elements are given by

$$\langle nsl, n'sl'; SL | H_{el} | n''sl'', n'''sl'''; SL \rangle =$$

$$\sum_t (-1)^{l'+l''} \Big[(-1)^L \begin{Bmatrix} l''' & l'' & L \\ l & l' & t \end{Bmatrix} (l||C^{(t)}||l'')(l'||C^{(t)}||l''') \times$$
$$\times R^{(t)}(nln'l';\ n''l''n'''l''') +$$

$$+ (-1)^S \begin{Bmatrix} l'' & l''' & L \\ l & l' & t \end{Bmatrix} (l||C^{(t)}||l''')(l'||C^{(t)}||l'')R^{(t)}(nln'l';$$

$$n'''l'''n''l'')\Big]$$

where $C^{(t)}$ are tensor operators related to the usual spherical harmonics, the $R^{(t)}$ are the Slater radial integrals. For a two-electron configuration, $nl \equiv n''l''$ and $n'l' \equiv n'''l'''$, the Slater integrals $R^{(t)}$ are usually denoted

$$R^{(t)}(nln'l';\ nln'l') \equiv F^{(t)}(nl;n'l')$$

and $R^{(t)}(nln'l';\ n'l'nl) \equiv G^{(t)}(nl;n'l')$

The magnetic part for the two-electron configuration of (3.1) can be evaluated with use of the formulae

$$\langle nsl,\ n'sl';\ SLJM|H_{magn}|nsl,\ n'sl';\ S'L'J'M'\rangle =$$

$$= \delta(J,J')\delta(M,M')\ (-1)^{l+l'+S'+L+J+1}[S,S',\ L,\ L']^{1/2}\ \times$$

$$\times \begin{Bmatrix} S & S' \\ L' & L \end{Bmatrix} \begin{Bmatrix} 1 & S & S' & 1 \\ J & 1/2 & 1/2 & 1/2 \end{Bmatrix} (3/2)^{1/2}\ \times$$

$$\times \Big[(l(l+1)(2l+1))^{1/2} \begin{Bmatrix} L & L' & 1 \\ l & l & l' \end{Bmatrix} (-1)^{S'+L'} \zeta_{nl}\ +$$

$$+\ (l'(l'+1)(2l'+1))^{1/2} \begin{Bmatrix} L & L' & 1 \\ l' & l' & l \end{Bmatrix} (-1)^{S+L}\ \zeta_{n'l'} \Big]$$

where ζ_{nl} is the spin-orbit parameter [12] defined as

$$\zeta_{nl} = \int_0^\infty R^2_{nl}(r)\,\xi(r)\ dr.$$

Second-order effects on the term structure of the configuration nln'l' can be taken account by including the effective Hamiltonian

$$H^{(2)}_{eff} = \vec{l}\cdot\vec{l}'\alpha + \vec{s}\cdot\vec{s}'\ \beta \qquad (3.2)$$

where α and β are adjustable parameters. Such effects play a role for the 6p6d configuration only. In the configurations npn's the effects of interactions with distant configurations are absorbed by the parameters $F^{(o)}$ and $G^{(1)}$. All parameters used for the parametrization of the fine structure interactions for the $6s^2 6p6d+6p^2 6p7s+6s^2 6p8s$ are given in Table 1. The computer program[+] used for the calculations uses coefficient matrices obtained before by means of Hamiltonians (1) and (2), and varies the values of fine structure parameters up to best agreement between the observed energy levels and the computed eigenvalues of the energy matrices by minimizing the χ^2/F.

As indicated above there are some problems to define an experimentally well confirmed set of energy levels. From the 6p6d configuration in Pb I 12 levels are arising, but only six are known with sufficient accuracy [6]. Two levels (at 60205

[+] We thank Dr. S. Büttgenbach for supplying the computer program.

and 61213 cm^{-1} with J = 1) are placed by Garton and Wilson [4] above the first ionization limit (59819 cm^{-1}). They show autoionized features [14] and their energy position might be inaccurate [15]. Following early suggestions [8,4] and in contrast to Brown et al. [5] we assumed the 6p6d ^3P_o level at 60482 cm^{-1}. We follow also the suggestion [4] to locate the 6p6d $^3P_2$ level at 60075 cm^{-1}. This is supported by an observed [5] line with 49423.52 cm^{-1} which can be classified as the $6s^2 6p^2\ ^3P_2 \rightarrow 6s^2 6p6d\ ^3P_2$ transition. Wood and Andrew [6] identified the 6p6d $^3D_3$ level at 59186.62 cm^{-1} where as the results for the $^3D_3$ and $^3P_1$ level given in Ref. 2 could not be confirmed by later work [4,5,6]. We assume the 6p8s $^3P_2$ level at 62620.9 cm^{-1}, following Ref. 2 although this level is not mentioned in Refs. 4,5 and 6. Two observed, but unclassified lines [5] with 51970.94 cm^{-1} and 54801.88 cm^{-1} can be ascribed to the $6s^2 6p^2\ ^3P_1 \rightarrow 6s^2 6p8s\ ^3P_2$ and the $6s^2 6p^2\ ^3P_2 \rightarrow 6s^2 6p8s\ ^3P_2$ transition, respectively, supporting our assumptions. The autoionized 6p8s $^3P_1$ level showed some difficulties when fitting the fine structure, most likely due to a pertubation originating from the unidentified $6s6p^3$ configuration [16]. In the final fit the 6p8s $^3P_1$ has been omitted.

Tab. 2 presents the levels considered in our analysis. We need 19 parameters for describing the 6p6d + 6p7s + 6p8s configurations including five parameters representing off-diagonal interactions. However, the energy position of only 17 levels are known. Therefore, we have to introduce some additional information about the g-factors (given in Ref. 9). Racah [17] has shown that off-diagonal Slater integrals $R^1(ld,sl)$ are limited by

$$|R^1(ld,sl)| \leq [G^1(ld) \cdot G^1(ls)]^{1/2} \tag{3.3}$$

which gives constraints for $|R^{(1)}(6p6d, 6p7s)|$, $|R^{(1)}(6p6d,6p8s)|$ and $|R^{(1)}(6p7s,6p8s)|$:

$$|R^{(1)}(6p6d,7s6p)| \leq [G^{(1)}(6p6d) \cdot G^{(1)}(6p7s)]^{1/2} \tag{3.4}$$

$$|R^{(1)}(6p6d,8s6p)| \leq [G^{(1)}(6p6d) \cdot G^{(1)}(6p8s)]^{1/2} \tag{3.5}$$

$$|R^{(1)}(6p7s,8s6p)| \leq [G^{(1)}(6p7s) \cdot G^{(1)}(6p8s)]^{1/2} \qquad (3.6)$$

For the radial integrals connecting the configuration 6p8s with 6p6d, or 6p7s, we assumed on the basis of eq.3.2 as follows:

$$R^{(1)}(6p6d,8s6p) = \left[\frac{G^{(1)}(6p8s)}{G^{(1)}(6p7s)}\right]^{1/2} R^{(1)}(6p6d,7s6p) \qquad (3.7)$$

and by analogy

$$R^{(2)}(6p6d,6p8s) = \left[\frac{G^{(1)}(6p8s)}{G^{(1)}(6p7s)}\right]^{1/2} R^{(2)}(6p6d,6p7s) \qquad (3.8)$$

We have observed that the g-factor of the 6p6d $^3F_2$ level is very sensitive to the value of the Slater integral $F^{(2)}(6p6d)$. We varied this value stepwise up to sufficient agreement between experimental and calculated g-factors. Likewise, preserving this agreement and using relations (3.4 - 3.6) we fitted the off-diagonal Slater integrals $R^{(1)}$ and $R^{(2)}$.

4. Hyperfine structure analysis and evaluations of one-electron parameters

For configurations of the type nln'l', we have to study the effective Hamiltonian for the magnetic-dipole interaction [18]

$$H_{hfs}(M1) = I \cdot [\sum_{nl} a^{01}_{nl}\, \vec{l} + a^{12}_{nl} (\vec{s} \times \vec{C}^{(2)})^{(1)} + a^{10}_{nl}\, \vec{s}], \qquad (4.1)$$

and for electric-quadrupole interaction [18]

$$H_{hfs}(E2) = \frac{T_n^{(2)}}{eQ} \left[\sum_{nl} b^{02}_{nl} \left(\frac{2l(l+1)(2l+1)}{(2l-1)(2l+3)}\right)^{1/2} u^{(02)2} + \left(\frac{3}{10}\right)^{1/2} b^{13}_{nl}\, u^{(13)2} + \left(\frac{3}{10}\right)^{1/2} b^{11}_{nl}\, u^{(11)2} \right] \qquad (4.2)$$

The quantities $a^{\kappa k}_{nl}$ and $b^{\kappa k}_{nl}$ are one-electron parameters and will be treated as free parameters.

Some of the parameters are common to several configurations, so that comparisons are of interest. In general, however, we should not expect, that equivalent parameters take exactly the same values, since a particular electron will experience slightly different fields due to configuration interaction and changes in shielding (see slightly different values for the spin-orbit parameter ζ_p in the configurations 6p6d,6p7s and 6p8s, Table 1). Likewise, the parameters $a^{\kappa k}_{6p}$ appearing in the three configurations can be slightly varying.

In our case, where we consider the configuration 6p6d + 6p7s+6p8s the Hamiltonians (4.1) and (4.2) have as well non-vanishing matrix elements between configurations

6p6d and 6p7s, or 6p8s and 6p7s and 6p8s.

Therefore, with Hamiltonian (4.1) three additional parameters for the magnetic-dipole interaction are introduced

$$a^{12}_{6dn's} = 2\mu_B g_I \, (1+\Delta^{12}_{6dn's}) \, \langle 6d|r^{-3}|n's\rangle \, F^{12}_{6dn's} \qquad (4.3)$$

(n' = 7, or 8)

$$a^{10}_{7s8s} = \frac{16\pi}{3} \mu_B g_I \, \psi_{7s}(o)\psi_{8s}(o) F^{10}_{7s8s} \quad , \qquad (4.4)$$

Similarly with Hamiltonian (4.2) the parameters for the quadrupole interaction

$$b^{o2}_{6dn's} = e^2 Q(1+\Delta^{02}_{6dn's}) \, \langle 6d|r^{-3}|n's\rangle \, R^{o2}_{6dn's} \qquad (4.5)$$

(n' = 7, or 8)

appear where $\Delta^{12}_{6dn's}$ and $\Delta^{o2}_{6dn's}$ represent second-order contributions from excitation from full shells to empty shells [19]. $F^{\kappa k}$ and $R^{\kappa k}$ are relativistic correction factors (RCF) [20].

The values of the radial parameters $\langle 6d|r^{-3}|n's\rangle$ are expected to be very small. Consequently effects represented by the parameters $a^{12}_{6dn>s}$ and $b^{o2}_{6dn>s}$ have been neglected in our calculations.

In second and higher orders, however, there are others nonvanishing matrix elements between the configurations pd and ps, which have the angular dependence of three operators $\vec{t}^{01}$, $\vec{t}^{12}$ and $\vec{t}^{10}$ appearing in Hamiltonian (4.1) and therefore lead to screening of the corresponding parameters a^{01}, a^{12} and a^{10} in both configurations. The importance of their influence on a^{01} and a^{12} seems to be much smaller as the influence on the Fermi term a^{10}. Therefore, we would discuss at this work a off-diagonal core-polarization effect only. A similar effect has been found to be very significant in the $(3d+4s)^{N+2}$ configurations [21].

The excitations

$$6s^2 6p6d \xleftrightarrow{\vec{G}} 6s^2 6pn'''s \xleftrightarrow{\vec{t}^{1o}} 6s^2 6p7s$$

lead to the following two-body contributions δA^{1o}_J to the effective hfs matrix in the $6s^2 6p6d$ + $6s^2 6p7s$ space:

$$\delta(A^{10}_J) = -\sum_m \langle\phi_f|\vec{G}|m\rangle\langle m|\vec{t}^{(10)1}|\phi_i\rangle/\Delta E =$$

$$= (-1)^J\,\delta(L,1)\,\left(\frac{2J+1}{J(J+1)}\right)^{1/2} \begin{matrix} J & J & 1 \\ S' & S & L \end{matrix}\;[S,S']^{1/2}\left(\frac{3}{2}\right)^{1/2} \times$$

$$\times \left[-\left(\frac{1}{15}\right) a^{10}(pd,ps''') + (-1)^S \frac{1}{3} a^{10}(pd,s'''p)\right] \tag{4.6}$$

where $\vec{G}$ is the Coulomb operator and

$\phi_f = 6s^2 6p6d;SLJ$, $\phi_i \equiv 6s^2 6p7s;S'LJ$, $m = 6s^2 6pn'''s;S''L''J''$, and the $a^{10}(pd,pn'''s)$ and $a^{10}(pd,n'''sp)$ are new second-order hfs parameters which are defined as follows:

$$a^{10}(pd,ps''') = \frac{16\Pi}{3}\,\mu_\beta g_I \sum_{n''=8,9} (p||C^{(2)}||p)(d||C^{(2)}||s)\;\times$$

$$\times\; R^{(2)}(6p6d,6p\,n'''s)\,\psi_{7s}(0)\,\psi_{n'''s}(0)/\Delta E \tag{4.7}$$

$$a^{10}(pd,s'''p) = \frac{16\Pi}{3}\,\mu_\beta g_I \sum_{n''=8,9} (p||C^{(1)}||s)(d||C^{(1)}||p)\;\times$$

$$\times\; R^{(1)}(6p6d,n'''s\;6p)\,\psi_{7s}(0)\,\psi_{n'''s}(0)/\,\Delta E \tag{4.8}$$

Similar effects appear between the configurations 6p6d and 6p8s but the mixing between these configurations is much smaller and the Slater integrals $R^{(1)}$ and $R^{(2)}$ decrease with increasing n'''. Therefore, we have neglected these contributions. These are further diagonal and off-diagonal (electrostatically correlated) second-order hyperfine effects which are omitted in this work.

As indicated by Table 4 we need a total of 17 parameters for the parametrization of the hfs within the 6p6d + 6p6s + 6p8s model space. Unfortunately only 8 hfs A-constants are available. Therefore additional assumptions are necessary.

Following assumptions have been adopted in order to reduce the number of free parameters:

a) in all three configurations we take $a^{12}_{6p} / a^{10}_{6p} = 2$ suggested by relativistic Hartree-Fock calculations (RHF) [20] (the value of this ratio has been confirmed for the Bi atom and ion [22,23]),

b) a^{01}_{6p} (6p6d): a^{01}_{6p} (6p7s): a^{01}_{6p} (6p8s) =

= ζ_{6p} (6p6d): ζ_{6p}(6p7s): ζ_{6p}(6p8s) =

= 1 : 0.9721 : 1.0227

c) $a^{12}_{6d} / a^{01}_{6d} = 1.33$ according to RHF calculations,

d) $a^{10}_{7s8s} = \sqrt{a^{10}_{7s} \cdot a^{10}_{8s}}$

e) $a^{10}(pd,ps''')$ / $a^{10}(pd,s'''p) = -1.62$ according to our Hartree-Fock estimation

f) $a^{10}_{6p}(6p6d) = a^{10}_{6p}(6p7s) = a^{10}_{6p}(6p8s)$.

The assumption (f) is most questionable, because the experimental value a^{10}_{nl} (l>0) is the sum of the relativistic effects and the core-polarization contribution due to the Fermi contact term. Both contributions can be slightly different in the considered configurations.

Finally, we fitted eight theoretical expressions for the A-constants to eight experimental A values available for the isotop ^{207}Pb using seven free parameters. The results of the fitting procedure are given in Table 4.

In order to check the introduced assumptions, we studied their influence replacing assumption (b) e.g. by

$$a^{01}_{6p}(6p6d) = a^{01}_{6p}(6p7s) = a^{01}_{6p}(6p8s)$$

The best-fit obtained was significantly worse. Omitting the assumption (a) leads to a linear dependence between terms with a^{12}_{6p} and a^{10}_{7s}. It is interesting to note that fits neglecting off-diagonal terms between the three configurations give a non-acceptable negative value of the parameter a^{10}_{8s}. This indicates the existance of hfs interactions between the configurations 6p6d, 6p7s and 6p8s.

5. Test of the results by expectation from systematics

Our hfs analysis has been performed with many assumptions hampered by lack of experimental data. However, we can additionally introduce arguments from the systematics within 6p-elements. A test is provided by a ratio of the spin-orbit parameter ζnl by the hfs orbital parameter $\langle r^{-3}\rangle_{nl}^{01}$. The $\langle r^{-3}\rangle_{nl}^{01}$ can be obtained from experimental one-electron parameter using the relation [20] (a_{nl}^{01} in MHz and $\langle r^{-3}\rangle_{nl}^{01}$ in a.u.):

$$a_{nl}^{01} = 95.4128\, g_I\, \langle r^{-3}\rangle_{nl}^{01} .$$

Moreover, from the definitions of the $\langle r^{-3}\rangle_{nl}^{01}$ and ζ_{nl}, we have [18,25]

$$\langle r^{-3}\rangle_{nl}^{01} = (1 + \Delta_{nl}^{01})\, \langle r^{-3}\rangle\, F_{nl}^{01} \tag{5.1}$$

and

$$\zeta_{nl} = \alpha^2\, R_\infty\, Z_i (1+\Delta_{nl}^{so}) \langle r^{-3}\rangle H_r \tag{5.2}$$

with α the fine structure constant, R_∞ the Rydberg constant, Z_i the effective atomic number, Δ_{nl}^{01} and Δ_{nl}^{so} second-order contributions originating from excitations of full shells to empty shells, which are identical in this case [25]; F_{nl}^{01} and H_r are relativistic correction factors.

Now, we can define a factor $\gamma\ (Z_{i,}A)$ as follows from Eqs. (5.1) and (5.2):

$$\gamma(Z_i,\ Z) = \zeta_{nl}/\langle r^{-3}\rangle_{nl}^{01} =$$

$$= \alpha^2\, R_\infty\, Z_i\, H_r\, /\, F_{nl}^{01} \tag{5.3}$$

or more illustrating

$$\gamma'(Z_i,\ Z) = \zeta_{nl}\, /\, (\alpha^2 R_\infty\, \langle r^{-3}\rangle_{nl}^{01}) =$$

$$= Z_i\, H_r\, /\, F_{nl}^{01} \tag{5.4}$$

Z denotes the atomic number.

From here, we can expected that the values γ' for the neighbouring ($Z_i(Z) - Z_i(Z')=1$) elements in region about $Z_i \approx 80$ should be very similar, because the F_{6p}^{01} increases, roughly, twice rapidly as the H_r and the ratios [20] $F_{6p,}^{01}(A)\ /\ F_{6p}^{01}(A')$ are slightly greater as the ratios $Z_i(Z)\ /\ Z_i(Z')$. In Table 6 we put together the experimental values of the one-electron parameters available for the atom and ion of bismuth and for the lead atom. Inspecting this table, we can conclude that the values found for the investigated configurations 6p6d, 6p7s and 6p8s are quite reasonable.

A comparison of the accurate γ' values for the $6p^3$ configuration in BiI with the corresponding values for the 6pn'l' configuration in PbI shows that the uncertainty of the values obtained in this work is within 6 percent. This will determine the theoretical uncertainty when evaluating experimental B-factors in terms of nuclear quadrupole moments.

6. Repulsion between hyperfine structure sublevels with the same quantum number F

The lead resonance transition 283.3 nm involves the levels $6p^2\ {}^3P_o$ and $6p7s\ {}^3P_1$. The lower level $6p_2\ {}^3P_o$ (with F = I) is very well separated from others. The nearest hfs sublevel with F = I has a distance of about 7819 cm^{-1} and this reduces the repulsion effect (below 0.01 MHz) very strongly. The upper level $6p7s\ {}^3P_1$ finds the first interacting level in a distance of 327 cm^{-1}. Therefore the repulsion effect could be expected to be significant. However, the exact intermediate coupling calculation shows that this effect remains rather small. This can be easily understood by inspecting the matrix elements of the intermediate coupling approximation. The main contribution to the second-order shift of the hfs sublevel $6p7s\ {}^3P_1$, F = I originates from interaction with the level $6p7s\ {}^3P_o$ with F = I. For the magnetic-dipole interaction the matrix elements are:

$$<ps\ {}^3P_o;FM\ |H_{hfs}(M1)|ps\ {}^3P_1I;FM> = \tag{6.1}$$

$$= (-1)^{2I} \begin{Bmatrix} I & I & 1 \\ 0 & 1 & I \end{Bmatrix} (I(I+1)(2I+1))^{1/2} \times$$

$$\times\ (\sqrt{2}/2)\ (-2a_p^{01} - a_p^{12} + a_p^{10} + a_s^{10}) \tag{6.2}$$

and

$$<ps\ {}^3P_oI,\ FM\ |H_{hfs}(M1)|\ ps\ {}^1P_1I;\ FM> =$$

$$= (-1)^{2I} \begin{Bmatrix} I & I & 1 \\ 0 & 1 & I \end{Bmatrix} (I(I+1)(2I+1))^{1/2}\ (-a_p^{10} + a_s^{10})/2 \tag{6.3}$$

In the first matrix element, we recognize the compensation of contributions from the 6p and 7s electrons. In addition, when including the eigenvector amplitudes (see Tab. 3) the contributions with the matrix elements $<^3P||H_{hfs}||^3P>$ and $<^3P||H_{hfs}||^1P>$ have different signs.

Finally, we can estimate the second-order shift for the different isotopes using the semi-empirical formula:

$$W^{(2)}(^3P_1, F = I) = 0.12\ g_I^2\ I\ (I + 1) \quad [\mathrm{MHz}]$$

The exact calculation gives a value of -0.12 MHz for the ^{207}Pb isotope. For the others isotopes the values are also within the experimental errors and vary from -0.006 MHz for the ^{202}Pb to -0.28 MHz for the ^{209}Pb. We can conclude that the repulsion between hfs sublevels has no essential influence on the values of the A- and B-constants and is unlikely to affect the positions of the gravity center of hfs components measured in Ref. 1.

Murakawa [10] observed on the 406.2 nm Pb-line unusual values of the odd-even staggering. He attributed this observation to the interaction of the initial 6p6d $^3D_1$ level with the 6p6d $^3F_2$ level, which is only 8 cm^{-1} apart. We cannot support this explanation by our calculations. Our intermediate coupling calculation gives for the sublevels with F = 3/2 (for the ^{207}Pb) a value smaller than 1 MHz, which is smaller than experimental error. Therefore, it can be assumed that the A-constant for the two above mentioned levels as given by Hüffer [9] must not be corrected for this effect.

7. Determination of the quadrupole moments of Pb nuclei from measured B-factors

In intermediate-coupling approximation the expression for the B-constant of the 6p7s $^3P_1$ level is as follows:

$$B(6p7s\ ^3P_1) = -0.021311\ b_{6p}^{02} + 0.004175\ b_{6p}^{11} \qquad (7.1)$$

The contributions to the B-constant from the 6d electron originating from mixing with the 6p6d configuration are very small and have been neglected.

The effective hfs one-electron parameters, in absence of configuration interaction, are connected to the nuclear quadrupole moment Q in the following way [20] ($b^{\kappa k}$ in MHz, $\langle r^{-3}\rangle^{\kappa k}$ in a.u., Q in barn):

$$b^{\kappa k}_{nl} = 234.974 \langle r^{-3}\rangle^{\kappa k}_{nl} \, Q \qquad (7.2)$$

where κk = 02,11 for the p-electron.

From relativistic calculations (RHF) by Lindgren and Rosén [20], we have

$$\begin{aligned} b^{11}_{6p}/b^{02}_{6p} &= \langle r^{-3}\rangle^{11}_{6p}/\langle r^{-3}\rangle^{02}_{6p} = \\ &= R^{11}_{6p}/R^{02}_{6p} = -0.680 \end{aligned} \qquad (7.3)$$

and

$$\langle r^{-3}\rangle^{02}_{6p} \,/\, \langle r^{-3}\rangle^{01}_{6p} = 0.8262 \qquad (7.4)$$

Using eq. 7.4 and the value $\langle r^{-3}\rangle^{01}_{6p}$ for the 6p7s configuration from Table 6, we obtain:

$$\langle r^{-3}\rangle^{02}_{6p}(6p7s) = 20.3(1.2) \text{ a.u.} \qquad (7.5)$$

The error of 1.2 a.u. results from the discussion in sect. 5. By all this we find the semiempirical relation

$$Q(^{A}\mathrm{Pb}) = -0.00868(52) \quad B(^{A}\mathrm{Pb},\ 6p7s\ ^{3}P_{1}) \qquad (7.6)$$

Using the B-factors values given in Ref. 1, we have:

$Q\ (^{199}\mathrm{Pb}) = +\ 0.08\ (8)$ [b]
$Q\ (^{201}\mathrm{Pb}) = -\ 0.009\ (90)$ [b]
$Q\ (^{202m}\mathrm{Pb}) = +\ 0.58\ (15)$ [b]
$Q\ (^{203}\mathrm{Pb}) = +\ 0.10\ (10)$ [b]
$Q\ (^{205}\mathrm{Pb}) = +\ 0.23\ (6)$ [b]
$Q\ (^{209}\mathrm{Pb}) = -\ 0.27\ (16)$ [b]

The obtained Q-values are about 40 % greater than those quoted in Ref. 1

8. Conclusion

Though there have been considerable efforts in analysing the fine- and hyperfine structure data of the Pb atom, the interpretation and the agreement with the observed data are not perfect in all details. Some deficiencies may be attributed to interactions with the unknown $6s6p^3$ configuration expected to be overlapping in the considered region. The unpaired 6s electron may strongly influence the hfs splitting and isotope shift. The odd-even staggering seen for the λ = 283.3 mm Pb I resonance line appears to be unaffected by the atomic structure. The unusual odd-even staggering of the 406.2 nm Pb I line [10] may have the same origin as the off-diagonal core-polarization effect discussed in sect. 6. The 6p6d $^3D_1$ level proves to be affected by admixtures from the 6p7s configuration (see Tab. 3). Therefore the contribution of the off-diagonal core polarization to the electron density at the nucleus is not negligible (see Ref. 27).

Using the results of the analysis we presented a semiempirical relation between B-factors of the 6p7s $^3P_1$ state in Pb I and nuclear quadrupole moments. From independent tests of our calculations we conclude that the theoretical uncertainty of this relation is within 6 %.

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Table 1 Fine structure parameters for the odd configurations in Pb I.

Parameter	Value [cm^{-1}]
$6s^26p6d$	
F^0	55262(311)
$F^2(6p,6d)$	5950
$G^1(6p,6d)$	2508(630)
$G^3(6p,6d)$	2587(700)
ζ_p	9075(40)
ζ_d	90(60)
α	-29(15)
β	289(140)
$6s^26p7s$	
F^0	44469(133)
$G^1(6p,7s)$	694(83)
ζ_p	8822(54)
$6s^26p8s$	
F^0	58174.
$G^1(6p,8s)$	220(170)
ζ_p	9281(68)
Off-diagonal parameters	
$R^{(2)}(6p6d,6p7s)$	-4600.
$R^{(1)}(6p6d,7s6p)$	-2200.
$R^{(2)}(6p6d,6p8s)$	-2590.
$R^{(1)}(6p6d,8s6p)$	-1240.
$R^{(1)}(6p7s,8s6p)$	750.

Table 2 Observed and calculated energy levels of Pb I

Conf.	Desig.	J	Energy in cm^{-1}			g-factors		
			Observed	Calc.	O-C	Observed	Calc.	O-C
$6s^26p7s$	^3P	0	34959.908	34946	14			
		1	35287.224	35302	-15	1.3503[a]	1.3502	0.001
		2	48188.630	48193	- 4	1.496[b] 1.494[c]	1.4988	
	^1P	1	49439.616	49425	15	1.1076[a]	1.1096	0.0020
$6s^26p6d$	^3F	2	45443.171	45344	99	0.7921[a]	0.7919	0.0002
		3	46328.667	46261	68	1.1235[a]	1.1193	0.0042
		4		59421			1.2506	
	^1F	3		60321			1.0622	
	^3D	1	46068.438	46086	-18	0.8541[a]	0.8581	-0.0040
		2	46060.836	46216	-155	1.247[b] 1.251[c]	1.2427	
		3	59186.62	59295	-108		1.2361	
	^1D	2	58517.607	58642	-124	0.97[c]	0.9701	0.00
	^3P	0	60482	60546	-64			
		1	60205	60098	106		1.1010	
		2	60075	59921	154		1.3319	
	^1P	1	61213	61163	49		1.1651	
$6s^26p8s$	^3P	0	48726.262	48707	19			
		1	48686.934	48713	-26	1.304[b] 1.313[c]	1.3047	
		2	62620.9	62632	-11		1.5010	
	^1P	1		63385			1.1136	

a - Ref.9, b - Ref.2, c - Ref.7.

Table 3 SL-eigenvectors for the states under study of the configuration $6s^2 6p6d + 6s^2 6p7s + 6s^2 6p$ + 8s of the lead atom (energy of levels is in cm^{-1})

Real state / SL- -basis		6p7s $^3P_1$ E = 35287.	6p6d $^3D_1$ E = 46068.	6p8s $^3P_1$ E = 48687.	6p7s $^1P_1$ E = 49440	6p6d $^3F_2$ E = 45443.	6p6d $^3D_2$ E = 46061.	6p7s $^3P_2$ E = 48189	6p6d $^3F_3$ E = 46329.
$6s^2 6p6d$	^3F					0.826865	-0.274289	0.009385	0.689197
	^1F								0.535358
	^3D	-0.021844	0.685790	-0.041172	0.339612	-0.120703	0.629742	-0.059988	-0.488261
	^1D					0.515760	0.354924	-0.047106	
	^3P	0.003249	-0.361572	0.008596	-0.163349	-0.188157	-0.628460	0.044024	
	^1P	-0.064191	0.517559	-0.020894	0.065177				
$6s^2 6p7s$	^3P	0.836156	0.229013	0.204984	-0.452522	0.017623	0.084983	0.995927	
	^1P	0.544140	-0.259573	-0.337043	0.710110				
$6s^2 6p8s$	^3P	0.012029	-0.063145	0.753395	0.320179	0.001590	0.005989	0.016878	
	^1P	0.001277	-0.085307	0.523998	0.205391				

Table 4 Experimental values of the one-electron parameters for the configuration 6p6d+6p7s+6p8s in ^{207}Pb (in MHz)

Configuration 6p6d

$a^{01}_{6p} = 2825(82)$ $a^{12}_{6p} = 5650$ $a^{10}_{6p} = -2114(395)$

$a^{01}_{6d} = 69(62)$ $a^{12}_{6d} = 92$ $a^{10}_{6p} = 430(322)$

Configuration 6p7s

$a^{01}_{6p} = 2747$ $a^{12}_{6p} = 5494$ $a^{10}_{6p} = -2114$

$a^{10}_{7s} = 5821(222)$

Configuration 6p8s

$a^{01}_{6p} = 2889$ $a^{12}_{6p} = 5778$ $a^{10}_{6p} = -2114$

$a^{10}_{8s} = 2235(793)$

Off-diagonal parameters

$a^{10}_{7s8s} = 3607$

$a^{10}_{(pd,ps''')} = 7890(5100)$ $a^{10}_{(pd,s'''p)} = -4870$

Table 5 Results of the fit of theoretical expressions for the A_J constants to their experimental values for the ^{207}Pb (in MHz)

Level		$A_{exp.}$	$A_{calc.}$	$A_{exp.}-A_{calc.}$	$(A_{exp.}-A_{calc})/A_{exp.}$ in %
6p7s	$^3P_1$	8807.2(3.0)[a]	8822.6	- 15.7	- 1.7
6p6d	$^3D_1$	- 2988(8)[b]	-2904	- 84	2.8
6p8s	$^3P_1$	6009(60)[cd]	5876	133	2.2
6p7s	$^1P_1$	265(2)[b]	272	- 7	- 2.8
6p6d	$^3F_2$	3090(7)[b]	2972	118	3.8
6p6d	$^3D_2$	- 1700(5)[b]	-1703	3	- 0.2
6p7s	$^3P_2$	1956(60)[cd]	1745	211	10.8
6p6d	$^3F_3$	2080(5)[b]	2089	- 9	- 0.4

a = Ref. 1, b = Ref. 9, c = Ref. 10, d = Ref. 11.

Table 6 Valus of the one-electron radial parameters for the 6p-elements.

Element	Conf.	$\langle r^{-3}\rangle^{01}_{6p}$ in a.u.	$\langle r^{-1}\rangle^{12}_{6p}$ in a.u.	$\langle r^{-3}\rangle^{10}_{6p}$ in a.u.	$4\pi\lvert\psi_{ns}(0)\rvert^2 F^{10}_{ns}$ in a.u.	ζ_{6p} in cm^{-1}	$\gamma'(Z_i(Z))$ unitless
Bi I	$6s^2 6p^3$	29.33(10)[a]	59.94(14)[a]	-23.34(12)[a]	-	9959(10)[a]	58.1(2)
	$6s^2 6p^2 7s$	33.1(1.3)[b]	74.4(1.3)[b]	-25.8 (3)[b]	109.5(2.5)[b]	11560(540)[b]	59.7(2.5)
Bi II	$6s^2 6p^2$	35.4(3)[c]	72(1)[c]	-21(1)[c]	-	12001(10)[c]	58.0(6)
Pb I	$6s^2 6p^2$	21.1[d]	48.2[d]	-15.8[d]	-	7338(115)[e]	59.5(?)
	$6s^2 6p6d$	25.4(8)	50.8	-19.0(2.7)	-	9075(40)	61.1(3.5)
Pb I	$6s^2 6p7s$	24.6	49.2	-19.0	78.4(3.0)	8822(54)	61.1
	$6s^2 6p8s$	25.9	51.8	-19.0	30(11)	9281(68)	61.1

a = Ref. 23, b = a mean value from versions I and II in Ref. 26, c = Ref. 22, e = Ref. 7