Relativistic energy shifts in Ge II, Sn II and Pb II and search for cosmological variation of the fine structure constant

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Sensitivity of atomic transition frequencies to variation of the fine structure constant \(\alpha = e^2/\hbar c\) increases proportional to \(Z^2\) where \(Z\) is the nuclear charge. Recently several lines of heavy ions Ge II, Sn II and Pb II have been detected in quasar absorption spectra. We have performed accurate many-body calculations of \(\alpha^2\)-dependence of transition frequencies (\(q\)-coefficients) for these atoms and found an order of magnitude increase in sensitivity in comparison with atomic transitions which were previously used to search for temporal and spatial variation of \(\alpha\) in quasar absorption systems. An interesting feature in Pb II is highly non-linear dependence on \(\alpha^2\) due to the level pseudo-crossings.

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I. INTRODUCTION

Theories unifying gravity with other interactions suggest a possibility of temporal and spatial variation of fundamental constants of Nature. A review of these theories and measurement results can be found in [1]. A very sensitive many-multiplet (MM) method to search for the variation of the fine structure constant \(\alpha = e^2/\hbar c\) by comparison of quasar absorption spectra with laboratory spectra has been suggested in ref [2]. It requires calculations of relativistic corrections to atomic energy levels which allow one to find dependence of atomic transition frequencies on \(\alpha\):

\[
\omega = \omega_0 + qx
\]

(1)

where \(x = \alpha^2/\alpha_0^2 - 1 \approx 2\delta\alpha/\alpha\). Here \(\omega_0\) and \(\alpha_0\) are the laboratory values, \(\omega\) and \(\alpha\) are the rest value of transition frequency and the fine structure constant for an atom or ion in a remote cloud of ionized gas located on a distance up to 12 billion light years from us. Calculations of \(q\) for a number of atomic transitions have been performed in Refs. [3, 4, 5, 6]. Webb et al. [7] used MM method [2] and found possible evidence of \(\alpha\) variation, while other groups [11, 12] have used the same method [2] but found no indications of the variation (Note, however, that works [3, 4, 10] are based on data from Keck telescope located in Northern hemisphere while works [11, 12] used data from Very Large Telescope located in Southern hemisphere. Therefore, the disagreement between the results, in principle, may be attributed to the spatial variation of \(\alpha\).)

To improve these results it would be very important to include into data analysis new atomic transitions where possible effects of \(\alpha\) variation are larger. Indeed, now systematic effects are at most comparable to the observed frequency shifts corresponding to value of \(\delta\alpha/\alpha = (-0.54 \pm 0.12) \cdot 10^{-5}\) reported in [10]. If transitions with an order of magnitude larger values of \(q\) will be used these systematic effects will be negligible in comparison with the frequency shifts produced by \(\delta\alpha/\alpha = -0.5 \cdot 10^{-3}\).

Coefficients \(q\) are small in light atoms and rapidly increase (\(\sim Z^2\)) with nuclear charge \(Z\). Recently transitions in heavy ions Ge II \((Z = 32, \text{rest wavelength } 1602.4863 \text{ A})\), Sn II \((Z = 50, \text{rest wavelength } 1400.450 \text{ A})\) and Pb II \((Z = 82, \text{rest wavelength } 1433.9056 \text{ A})\) have been observed in quasar absorption spectra [8, 9]. Therefore, in the present work we perform calculations of the dependence of transition frequencies on \(\alpha\) in Ge II, Sn II and Pb II. Coefficients \(q\) in Pb II are an order of magnitude larger than in lighter elements \((Z < 31)\) which were studied in Refs. [3, 4, 5, 10, 11, 12]. Potentially, this may give an order of magnitude increase of sensitivity to \(\alpha\) variation and help to eliminate possible disagreement between the results of different groups.

Note that only E1 transitions from the ground states are observed in quasar absorption spectra.

II. CALCULATIONS

Calculations for Ge II, Sn II and Pb II are difficult due to strong configuration mixing and level pseudo-crossing. As it was pointed out in our previous works energies of different atomic states considered as functions of \(\alpha^2\) may have very different slopes and come to crossing at particular values of \(\alpha\) [4]. Since there can be no real crossing of levels with the same conserving quantum numbers the phenomenon is called level pseudo-crossing. Configurations are strongly mixed and the slope of curve representing \(E(\alpha^2)\) change very quickly in the vicinity of level pseudo-crossing. If this happens near physical value of \(\alpha\) \((\alpha \approx \alpha_0)\) the results for the coefficients \(q\) (see Eq. (1)) become unstable since small error in a position of level crossing results in a large error in \(q\). One way of dealing with this problem is by fitting the experimental values of the Landé \(g\)-factors [4]. When states of different total angular momentum \(L\) and total spin \(S\) are mixed...
the resulting values of \( g \)-factors depend on configuration mixing similar to \( q \)-coefficients (\( q \approx \sum q_i W_i \), \( g \approx \sum g_i W_i \) where \( W_i \) is the weight of a state \( i \)). Therefore, correcting the mixing coefficients to fit the experimental \( g \)-factors helps to find true values of the \( q \)-coefficients as well. However, in the case of ions considered in present work, there is strong configuration mixing between states of the same \( L, S \) and \( J \) (\( J \) is the total momentum). These states are the \( ^2D_J \) states of the \( ns^2 nd \) and \( nsnp^2 \) configurations (\( n = 4 \) for Ge II, \( n = 5 \) for Sn II and \( n = 6 \) for Pb II). The mixed states have the same values of \( g \)-factors and resulting \( g \)-factor does not depend on configuration mixing. In contrast, the values of \( q \)-coefficients are still sensitive to configuration mixing.

In principle, it is possible to use experimental hyperfine structure (hfs) to fit the configuration mixing coefficients. Since single-electron matrix elements of the hyperfine interaction have very different values for \( s, p \) and \( d \) states, different configurations must have different values of the many-electron hfs matrix element. Therefore, fitting the experimental hfs would have the same effect as fitting of experimental \( g \)-factors. Unfortunately, no experimental data on hfs is available for Ge II, Sn II and Pb II.

This leaves us with energies being the only control of the accuracy of calculation of the \( q \)-coefficients (with exception of few levels of Pb II where \( g \)-factors are also useful). Calculations need to be done to very high accuracy for the energies to be a reliable control. 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. The interval between different \( ^2D_J \) states of Ge II, Sn II and Pb II is a little larger than 10000 cm\(^{-1} \). Therefore, the deviation of the calculated energies from the experiment should be less than \( \sim 1000 \) cm\(^{-1} \) or \( < 1 \% \) of the excitation energy from the ground state.

A method which can produce the results of desirable accuracy was suggested in Ref. \[14\]. Calculations are done in the \( V^{N-3} \) approximation. This means that the self-consistent Hartree Fock procedure is done for the quadruply charged positive ion. As it has been demonstrated in Ref. \[14\], removal of \( s \) and \( p \) valence electrons doesn't really affect the atomic core (apart from single-electron energies) and \( V^{N-4} \) approximation is a good approximation for all ions with number of valence electrons ranges from 1 to 5. These include neutral atom and negative ion. The main advantage of this approximation is that core-valence correlations can be relatively easily included beyond the second-order of the perturbation theory. As it has been demonstrated in Ref. \[14\] inclusion of higher-order core-valence correlations can significantly improve the accuracy of calculations.

The ions of our current interest have three valence electrons and the effective Hamiltonian for the three-electron wave function of valence electrons has the form

\[
\hat{H}^{\text{eff}} = \sum_{i=1}^{3} \hat{h}_i + \sum_{i \neq j}^{3} \hat{h}_{2ij}, \tag{2}
\]

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

\[
\hat{h}_1 = c ap + (\beta - 1)mc^2 - \frac{Ze^2}{r} + V^{N-4} + \hat{\Sigma}_1. \tag{3}
\]

\( \hat{\Sigma}_1 \) is the single-electron operator (correlation potential) which describes correlations between a particular valence electron and core electrons. It is the same operator which is used for atoms and ions with one external electron above closed shells (see, e.g. \[12\], \[15\], \[17\]). \( \hat{h}_2 \) is the two-electron part of the Hamiltonian

\[
\hat{h}_2 = \frac{e^2}{|r_1 - r_2|} + \hat{\Sigma}_2(r_1, r_2), \tag{4}
\]

\( \hat{\Sigma}_2 \) is the two-electron part of core-valence correlations. It represents screening of Coulomb interaction between valence electrons by core electrons.

Note that removing \( \hat{\Sigma} \) from the effective Hamiltonian reduces it to the effective Hamiltonian of the standard configuration interaction (CI) method. Since we use many-body perturbation theory to calculate \( \hat{\Sigma} \) the technique we use can be called the CI+MBPT method \[13\].

The details of calculations for positive ions of Ge, Sn and Pb will be presented elsewhere. Below we discuss specifics of calculations for Ge II, Sn II and Pb II.

## A. Ge II

The Ge II ion is the lightest of three ions (\( Z=32 \)) and the easiest from computational point of view. The core-valence correlations are relatively small due to small number of electrons in the core. The relativistic corrections are small too. The latter means in particular that fine structure is small and energy multiplets stay well apart from each other and there is no level pseudo-crossing. Also, there is almost no mixing between states of different total angular momentum \( L \) and/or different total spin \( S \). The \( ^2D_{3/2,5/2} \) states of the \( 4s^24d \) and \( 4s4p^2 \) configurations are still strongly mixed. However, due to high accuracy of the calculations the final results are very stable.

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. The final results are presented in Table \[11\] to calculate \( q \)-coefficients (see Eq. \[11\]) we perform calculations of the energies for \( x = -0.1, 0, +0.1 \). Than \( q_+ = 10(\omega(0.1) - \omega(0)) \), \( q_- = 10(\omega(0) - \omega(-0.1)) \) and finally \( q = (q_+ + q_-)/2 \). We need both \( q_+ \) and \( q_- \) to check for non-linear behavior of energies which is usually an indicator of the level pseudo crossing. For Ge II \( q_+ \) and \( q_- \) are practically identical for all levels considered.
TABLE I: Energy levels and relativistic energy shift of Ge II (cm$^{-1}$).

| State | Energies | q |
|-------|----------|---|
| $4s^24p$ $^2P_{3/2}$ | 1767.1 | -1863 |
| $^2P_{1/2}$ | 1797 |
| $4s4p^2$ | 51575.5 | -3098 |
| $^2P_{3/2}$ | 51512 |
| $^4P_{1/2}$ | 52290.5 | -3901 |
| $^2P_{1/2}$ | 52241 |
| $^4P_{3/2}$ | 53366.7 | -5001 |
| $^2P_{5/2}$ | 53342 |
| $4s^25s$ $^2S_{1/2}$ | 62402.4 | -664 |
| $^2D_{5/2}$ | 65015.0 |
| $^2D_{3/2}$ | 65184.1 |
| $4s^25p$ | 79006.2 | -3612 |
| $^2P_{1/2}$ | 79386 |
| $^2P_{3/2}$ | 79658.8 |
| $^2P_{5/2}$ | 79750 | -5904 |
| $4s4p^2$ | 80363.1 | -2236 |
| $^2D_{5/2}$ | 81011.8 |

Table II: Energy levels and relativistic energy shift of Sn II (cm$^{-1}$).

| State | Energies | q |
|-------|----------|---|
| $5s^25p$ $^2P_{1/2}$ | 4251.4 | -4680 |
| $^2P_{3/2}$ | 4222 |
| $5s5p^2$ | 46464.2 | -5930 |
| $^4P_{1/2}$ | 46661 |
| $^4P_{3/2}$ | 48368.0 |
| $^4P_{5/2}$ | 48556 | -8343 |
| $5s^26s$ $^2S_{1/2}$ | 56885.9 | -2679 |
| $^2D_{3/2}$ | 57892.8 |
| $^2D_{5/2}$ | 57920.0 |
| $5s5p^2$ | 58438.3 | -7361 |
| $^2D_{3/2}$ | 58806.0 |
| $^2D_{5/2}$ | 59355 |
| $5s^25d$ | 59463.4 | -8955 |
| $^2D_{5/2}$ | 59419 |
| $^2D_{3/2}$ | 59519 | -8325 |
| $5s^26p$ | 72047.6 | -7015 |
| $^2P_{3/2}$ | 71804 |
| $^2P_{1/2}$ | 71828 | -3119 |
| $2^2P_{1/2}$ | 72377.3 |
| $2^2P_{3/2}$ | 72861 | -4071 |

C. Pb II

The Pb II ion ($Z = 82$) is the most difficult for calculations. Correlations are strong and relativistic effects are large too. Strong $L - S$ interaction lead 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 Pb II to further improve the accuracy of calculations as compared to the scheme used for Sn II. We have introduced the scaling factors before $\Sigma_1$ 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

$$(\hat{H}_0 + \Sigma_1 - \epsilon_n)\psi_n = 0.$$ (5)

Here $\hat{H}_0$ is the Hartree Fock Hamiltonian. $\Sigma_1$ is the all-order correlation potential operator similar to what is used for Sn II. Inclusion of $\Sigma_1$ 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%. To further improve the energies we replace $\Sigma_1$ by $f \Sigma_1$ with rescaling factor $f$ chosen to fit the energies exactly. Then the same rescaled operator $f \Sigma_1$ is used for the Pb II ion. It turns out that only small rescaling is needed. Maximum deviation of the rescaling factor from 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 rescaling of the $\Sigma_1$ operator has similar effect on both ions Pb IV and Pb II (and Pb III) improving agreement with experiment in all cases. Although, the effect on the energies of Pb II is small, it is important due to the level crossing and strong configuration mixing which can make the results to be very unstable if the accuracy of calculations is not high enough.

Note that we fit the energies of Pb IV but not Pb II. The calculations for Pb II can be still considered as pure ab initio calculations since no experimental information about Pb II is used.

The results are presented in Table II. We also present on Fig. 1 the behavior of Pb II energy levels as functions of $(\alpha/\alpha_0)^2$. Dotted lines correspond to states with $J = 1/2$, short dash lines correspond to $J = 3/2$ and long dash lines correspond to $J = 5/2$ (the longer the dash the larger the $J$). Horizontal dashes on the right represent experimental energies.

The resulting picture is very complicated. There are at least three level pseudo-crossing. One is for the $^2D_{5/2}$ and $^2P_{3/2}$ states at about $(\alpha/\alpha_0)^2 = 0.8$, another is for the $^4P_{1/2}$ and $^2S_{1/2}$ states for $(\alpha/\alpha_0)^2 > 1$ and the third
TABLE III: Energy levels and relativistic energy shift of Pb II (cm$^{-1}$).

| State       | Energies | $q$          | Expt.$^a$ | Calculations |
|-------------|----------|--------------|-----------|--------------|
| 6s$^2$6p    | $^2P'_3/2$| 14081        | 0         | 0            |
|             | $^2P'_5/2$| 57911        | 0         | -21000       |
| 6s6p$^2$    | $^2P'_3/2$| 66124        | 0         | -34500       |
|             | $^2P'_5/2$| 73905        | 0         | -40700       |
| 6s$^2$7s    | $^2S'_1/2$| 59448        | 0         | -6800        |
| 6s$^2$6d    | $^2D'_3/2$| 68964        | 0         | -43000       |
|             | $^2D'_5/2$| 69740        | 0         | -14600       |
| 6s$^2$7p    | $^2P'_3/2$| 74459        | 0         | -8180        |
|             | $^2P'_5/2$| 77272        | 0         | -12240       |
| 6s6p$^2$    | $^2D'_3/2$| 83083        | 0         | -45200       |
|             | $^2D'_5/2$| 88972        | 0         | -46700       |

$^a$Moore, [13]

one is for the $^4P_{3/2}$ and $^2D_{3/2}$ states at $(\alpha/\alpha_0)^2 > 1$. In fact, due to the level pseudo-crossing, these states are so strongly mixed that their assignment to particular $L - S$ multiplets and configurations is ambiguous.

To improve the accuracy in $q$ we used experimental information about the $g$-factors and energy intervals between the strongly mixed levels. These values are reproduced with high accuracy in the interval of $(\alpha/\alpha_0)^2$ between 0.9 and 1. Also, this interval is far from the positions of the level pseudo-crossings which happen at $(\alpha^2/\alpha_0) > 1$ and $(\alpha/\alpha_0)^2 \approx 0.8$. Therefore, the results are stable. In this situation we use $q_-$ as the best estimate of the $q$-values: $q = q_- = 10(\omega(0) - \omega(-0.1)) (\omega = \omega(x)$, where $x = (\alpha/\alpha_0)^2 - 1$). A deviation of $\mathbf{7} = (q_- + q_+)/2$ from $q_-$ gives us a reasonable accuracy estimate in this case, $\approx 10\%$. Note again that the energies are calculated with much higher accuracy.

III. CONCLUSION

We used combination of the many-body perturbation theory and configuration interaction method to calculate dependence of the energy levels on the fine-structure constant ($g$-coefficients). This dependence is due to the Dirac relativistic corrections (which are strongly modified by the many-body effects). As we found in our previous works the Breit interaction and QED radiative corrections are not important for the atoms of interest.

Calculations in Ge II and Sn II are straightforward and dependance of the transition frequencies on $\alpha^2$ is close to the linear one ($q_+ \approx q_-$. The accuracy of the energy level calculation in Ge II and Sn II is better than 1%, for the fine structure intervals the accuracy is better than 3%. Therefore, the errors in $q$ should not exceed 3%. The levels where $q$ are anomalously small may be an exception. For example, a conservative estimate of accuracy for the level with $\omega = 62402$ cm$^{-1}$ in Ge II where $q = -664$ cm$^{-1}$ is better than 10%. The value of $q$ for this level ($q = -607$ cm$^{-1}$) was also calculated in our previous work [12]. The present calculation is more accurate.

The case of Pb II is more complicated due to the level pseudo-crossing (as functions of $\alpha$). The dependence on $\alpha^2$ is highly non-linear (see Fig. 1). However, after taking into account the experimental information about the $g$-factors and intervals between energy levels the errors in $q$-values are reduced to $\approx 10\%$.

The values of $q$ in Sn II and especially Pb II are much larger than in the elements which were previously used to search for $\alpha$ variation where $q \sim 1000$ cm$^{-1}$. For the detected transitions $^2$D$_{3/2}$ Ge II ($Z = 32$, rest wavelength 1602.4863 A) $q = -660$ cm$^{-1}$, Sn II ($Z = 50$, rest wavelength 1400.450 A) $q = -5900$ cm$^{-1}$, and Pb II ($Z = 82$, rest wavelength 1433.9056 A) $q = -14600$ cm$^{-1}$. The largest (in absolute value) calculated $q$-coefficient in Pb II is $q \approx -45000$ cm$^{-1}$. This may give significant increase in sensitivity to the variation of $\alpha$.

IV. ACKNOWLEDGMENTS

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![FIG. 1: Energies of lowest even-parity multiplets of Pb II as functions of $\alpha^2$.](image-url)
[1] J-P. Uzan, Rev. Mod. Phys. 75, 403 (2003).
[2] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. Lett., 82, 888 (1999).
[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] J.C. Berengut, V.A. Dzuba, V.V. Flambaum, and M.V. Marchenko, Phys. Rev. A, 70, 064101 (2004).
[6] J.C. Berengut, V.A. Dzuba, V.V. Flambaum, and M.V. Marchenko, [physics/0408542](https://arxiv.org/abs/physics/0408542) submitted to Phys. Rev. A.
[7] J. K. Webb, V. V. Flambaum, C. W. Churchill, M. J. Drinkwater, and J. D. Barrow, Phys. Rev. Lett. 82, 884 (1999).
[8] J. K. Webb, M. T. Murphy, V. V. Flambaum, V. A. Dzuba, J. D. Barrow, C. W. Churchill, J. X. Prochaska, and A. M. Wolfe, Phys. Rev. Lett. 87, 091301 (2001).
[9] M. T. Murphy, J. K. Webb, V. V. Flambaum, V. A. Dzuba, C. W. Churchill, J. X. Prochaska, J. D. Barrow, A. M. Wolfe, Mon. Not. R. Astron. Soc. 327, 1208 (2001).
[10] M. T. Murphy, J. K. Webb, V. V. Flambaum, Mon. Not. R. Astron. Soc. 345, 609 (2003).
[11] R. Srianand, H. Chand, P. Petitjean, and B. Aracil, Phys. Rev. Lett., 92, 121302 (2004).
[12] R. Quast, D. Reimers, and S. A. Levashkov, Astron. Astrophysics 415, L7 (2004).
[13] J.K. Webb, private communication.
[14] V. A. Dzuba, [physics/0501032](https://arxiv.org/abs/physics/0501032) submitted to Phys. Rev. A.
[15] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B, 20, 1399 (1987).
[16] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, Phys. Lett. A, 140, 493 (1989).
[17] V. A. Dzuba, V. V. Flambaum, and J. S. M. Ginges, Phys. Rev. D, 66, 076013 (2002).
[18] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A, 54, 3948 (1996).
[19] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.), Circ. No. 467 (U.S. GPO, Washington, D. C., 1958), Vols. 1-3.