

The α -dependence of transition frequencies for ions Si II, Cr II, Fe II, Ni II, and Zn II

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(Dated: November 8, 2006)

We performed accurate calculation of α -dependence ($\alpha = e^2/hc$) of the transition frequencies for ions, which are used in a search for the variation of the fine structure constant α in space-time. We use Dirac-Hartree-Fock method as a zero approximation and then the many-body perturbation theory and configuration interaction methods to improve the results. An important problem of level pseudocrossing (as functions of α) is considered. Near the crossing point the derivative of frequencies over α varies strongly (including change of the sign). This makes it very sensitive to the position of the crossing point. We proposed a semiempirical solution of the problem which allows to obtain accurate results.

PACS numbers: 31.30.Jv, 06.20.Jr, 95.30.Dr

I. INTRODUCTION

Recently there was an intensive discussion of the possible space-time variation of the fine structure constant $\alpha = e^2/hc$ at the cosmological scale. The first evidence for such variation has been reported in [1, 2, 3, 4, 5, 6] from the analysis of the astrophysical data. These results are to be compared with the number of experimental upper bounds on this variation obtained from other astrophysical observations (see, e.g. [7, 8, 9]) and from the precision laboratory measurements [10, 11, 12]. Recently a number of new laboratory tests have been proposed (see, e.g. [13]). The analysis of the microwave background radiation can also give some restrictions on time variation of α as suggested in [14, 15, 16]. Implementations of the space-time variation of the fine structure constant to the theory of the fundamental interactions are discussed e.g. in Refs. [17, 18, 19, 20, 21, 22, 23] (see also discussion and references in [3]).

The most straightforward way to look for the variation of α is to measure the ratio of some fine structure interval to an optical transition frequency, such as $\omega(np_{1/2} \rightarrow np_{3/2})$ and $\omega(n's_{1/2} \rightarrow np_{3/2})$ [37]. This ratio can be roughly estimated as $0.2\alpha^2 Z^2$, where Z is the nuclear charge [24]. Therefore, any difference in this ratio for a laboratory experiment and a measurement for some distant astrophysical object can be easily converted into the space-time variation of α . However, as it was pointed out in [25], one can gain about an order of magnitude in the sensitivity to the α -variation by comparing optical transitions for different atoms. In this case the frequency of each transition can be expanded in a series in α^2 :

$$\omega_i = \omega_i^{(0)} + \omega_i^{(2)}\alpha^2 + \dots \quad (1a)$$

$$= \omega_{i,\text{lab}} + q_i x + \dots, \quad x \equiv (\alpha/\alpha_0)^2 - 1, \quad (1b)$$

where α_0 stands for the laboratory value of the fine struc-

ture constant. Note, that Eq. (1a) corresponds to the expansion at $\alpha = 0$, while Eq. (1b) — to the expansion at $\alpha = \alpha_0$. In both cases parameters $\omega_i^{(2)}$ and q_i appear due to relativistic corrections.

For a fine structure transition the first coefficient on the right hand side of (1a) turns to zero, while for the optical transitions it does not. Thus, for the case of a fine structure and an optical transition one can write:

$$\frac{\omega_{\text{fs}}}{\omega_{\text{op}}} = \frac{\omega_{\text{fs}}^{(2)}}{\omega_{\text{op}}^{(0)}}\alpha^2 + O(\alpha^4), \quad (2)$$

while for two optical transitions i and k the ratio is:

$$\frac{\omega_i}{\omega_k} = \frac{\omega_i^{(0)}}{\omega_k^{(0)}} + \left(\frac{\omega_i^{(2)} - \omega_k^{(2)}}{\omega_k^{(0)}} \right) \alpha^2 + O(\alpha^4). \quad (3)$$

Quite often the coefficients $\omega_i^{(2)}$ for optical transitions are about an order of magnitude larger than corresponding coefficients for the fine structure transitions $\omega_{\text{fs}}^{(2)}$ (this is because the relativistic correction to a ground state electron energy is substantially larger than the spin-orbit splitting in an excited state [25, 26]). Therefore, the ratio (3) is, in general, more sensitive to the variation of α than the ratio (2). It is also important that the signs of coefficients $\omega_i^{(2)}$ in (3) can vary. For example, for s - p transitions the relativistic corrections are positive while for d - p transitions they are negative. This allows to suppress possible systematic errors which “do not know” about the signs and magnitude of the relativistic corrections [25]. On the other hand, for many cases of interest, the underlying atomic theory is much more complicated for Eq. (3). In particular, the most difficult case corresponds to transitions to highly excited states of a multi-electron atom, where the spectrum is very dense. And this happens to be a typical situation for astrophysical spectra, in particular, for large cosmological red shifts. Corresponding atomic calculations have to account very accurately for the electronic correlations, which may affect such spectra quite dramatically.

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TABLE I: Final results for parameters q from Eq. (1) for Si II, Cr II, Fe II, Ni II, and Zn II. Estimated errors are in brackets.

Ion	Transition	ω_0 (cm $^{-1}$)	q (cm $^{-1}$)
Si II	${}^2P_{1/2}^o \rightarrow {}^2D_{3/2}$	55309.3365	520 (30)
	$\rightarrow {}^2S_{1/2}$	65500.4492	50 (30)
Cr II	${}^6S_{5/2} \rightarrow {}^6P_{3/2}^o$	48398.868	-1360 (150)
	$\rightarrow {}^6P_{5/2}^o$	48491.053	-1280 (150)
	$\rightarrow {}^6P_{7/2}^o$	48632.055	-1110 (150)
Fe II	${}^6D_{9/2} \rightarrow {}^6D_{9/2}^o$	38458.9871	1330 (150)
	$\rightarrow {}^6D_{7/2}^o$	38660.0494	1490 (150)
	$\rightarrow {}^6F_{11/2}^o$	41968.0642	1460 (150)
	$\rightarrow {}^6F_{9/2}^o$	42114.8329	1590 (150)
	$\rightarrow {}^6P_{7/2}^o$	42658.2404	1210 (150)
	$\rightarrow {}^4F_{7/2}^o$	62065.528	1100 (300)
	$\rightarrow {}^6P_{7/2}^o$	62171.625	-1300 (300)
Ni II	${}^2D_{5/2} \rightarrow {}^2F_{7/2}^o$	57080.373	-700 (250)
	$\rightarrow {}^2D_{3/2}^o$	57420.013	-1400 (250)
	$\rightarrow {}^2F_{5/2}^o$	58493.071	-20 (250)
Zn II	${}^2S_{1/2} \rightarrow {}^2P_{1/2}^o$	48481.077	1584 (25)
	$\rightarrow {}^2P_{3/2}^o$	49355.002	2490 (25)

The first calculations of the coefficients q from Eq. (1) for the transitions suitable for astronomical and laboratory measurements were done in Refs. [25, 26, 27, 28]. Here we present a new and more accurate calculations of the coefficients q for the transitions, which are currently used in the analysis of the astrophysical data. A full list of these transitions was given in [3]. We have not recalculated here the lightest and the most simple atoms Mg and Al, for which the previous calculation [25] should be sufficiently accurate and focused on more complicated ions Si II, Cr II, Fe II, Ni II, and Zn II. Our final results for them are given in Table I. Note, that here we use the single parameter q instead of two parameters q_1 and q_2 used in the earlier works and $q \equiv \partial\omega/\partial x|_{x=0} = q_1 + 2q_2$. Details of the calculations and discussion of the accuracy will be given in Sec. III. Before that we briefly address few theoretical points in Sec. II.

II. THEORY

In order to find parameters $q = \partial\omega/\partial x|_{x=0}$ in Eq. (1) we perform atomic calculations for three values of x : $x_- = -1/8$, $x_0 = 0$, and $x_+ = 1/8$. That allows us to determine q : $q = 4(\omega(x_+) - \omega(x_-))$ and also estimate the second derivative $\partial^2\omega/\partial x^2|_{x=0}$. The large value of the latter signals that interaction between levels is strong (level pseudocrossing), and there is a risk of large errors. For these cases further analysis was done as described below.

a. Relativistic calculations of multi-electron ions. In order to accurately account for the dominant relativistic effects we use the Dirac-Hartree-Fock approximation as a starting point for all calculations of atomic spectra. Though most of the calculations were done for the

Coulomb potential, we have also estimated Breit corrections by including the magnetic part of the Breit interaction in the self-consistent field [29].

The ions we are dealing with in this paper have from one to nine electrons in the open shells. For one valence electron in Zn II the Dirac-Fock V^{N-1} approximation already gives rather good results. On the next step the core-valence correlations can be accounted for by means of the many-body perturbation theory (MBPT). Already the second order MBPT correction allows to reproduce the spectrum with the accuracy, better than 1%, which is more than sufficient for our current purposes.

Other ions of interest to us have at least three valence electrons. Here the dominant correlation correction to transition frequencies corresponds to the valence-valence correlations. This type of correlations can be accounted for with configuration interaction (CI) method. If necessary, the core-valence correlations can be included within combined CI+MBPT technique [30]. The latter usually provides an accuracy of the order of 1% or better for the lower part of the spectra of atoms and ions with two or three valence electrons [30, 31, 32]. However, the accuracy of *ab initio* methods decreases with the number of valence electrons and with excitation energy. Indeed, for a large number of valence electrons and/or sufficiently high excitation energy the spectrum becomes dense and the levels with the same exact quantum numbers strongly interact with each other. The part of the spectrum of Fe II above 55000 cm $^{-1}$ and, to a somewhat lesser extent, the spectrum of Ni II represent this situation. Therefore, for these ions we developed a semiempirical fitting procedure, which is described below.

In order to have additional control of the accuracy of our CI we performed calculations for most of the ions with two different computer packages. One package was used earlier in Refs. [30, 32, 33] and another one was used in Refs. [3, 25, 26, 27, 28, 31]. The former package allows to construct flexible basis sets and optimize configuration space, while the latter allows for a larger CI space as it works with the block of the Hamiltonian matrix, which corresponds to a particular total angular momentum of atom J . When there were no significant difference between two calculations, we only give results obtained with the first package. Nevertheless, our final results presented in Table I are based on both calculations.

b. Semiempirical treatment of the strong interaction of levels: pseudo-crossing. In the nonrelativistic limit $\alpha \rightarrow 0$, all multi-electron states are accurately described by the LS -coupling scheme: $E_{\alpha \rightarrow 0} = E_{p,n,L,S,J}$, where $p = \pm 1$ is the parity and n numerates levels with the same p, L, S , and J . For sufficiently small values of α the LS -coupling holds and the energy has the form:

$$E_{p,n,L,S,J} = E_{p,n,L,S}^{(0)} + \left(\frac{\alpha}{\alpha_0}\right)^2 \left(C_{p,n,L,S} + \frac{1}{2} A_{p,n,L,S} [J(J+1) - L(L+1) - S(S+1)] \right), \quad (4)$$

where the first term in the parentheses gives the slope for the centre of the multiplet and the second term gives the fine structure. With growing α the multiplets start to overlap and when the levels with the same p and J come close, the pseudo-crossing takes place.

Near the pseudo-crossing the slope of the energy curves changes dramatically. If such crossing takes place at $x \approx 0$, where x is defined by Eq. (1), i.e. near the physical value of α , it can cause significant uncertainty in the values of parameters q .

Let us first analyze the behaviour of the slopes $q(x)$ in the vicinity of the pseudo-crossing in the two-level approximation. Consider two levels E_1 and E_2 which cross at $x = x_c$:

$$E_1 = q_1(x - x_c), \quad (5a)$$

$$E_2 = q_2(x - x_c). \quad (5b)$$

If the interaction matrix element between these two levels is V , the exact adiabatic levels will be

$$E_{a,b} = \frac{1}{2} \left((q_1 + q_2)(x - x_c) \pm \sqrt{(q_1 - q_2)^2(x - x_c)^2 + 4V^2} \right). \quad (6)$$

It is easy now to calculate the energy derivative in respect to x in terms of the mixing angle ϕ between unperturbed states 1 and 2:

$$\frac{\partial E_{a,b}}{\partial x} = \cos^2 \phi q_{1,2} + \sin^2 \phi q_{2,1}. \quad (7)$$

Note, that at the crossing the angle ϕ varies from 0 on one side through $\pi/4$ in the centre to $\pi/2$ on the other side, which leads to the change of the slope $q_a(x) = \partial E_a / \partial x$ from q_1 through $(q_1 + q_2)/2$ to q_2 . The narrow crossings with small V are particularly dangerous, as the slopes change very rapidly within the interval $\Delta x \approx V/|q_1 - q_2|$. Then, even small errors in the position of the crossing point x_c , or the value of V can cause large errors in $q_{a,b}$. In this model we assume that non-diagonal term $V = \text{const}$. For the real atom $V \propto \alpha^2$. However, if the crossing region $\Delta x \ll 1$, we can neglect the dependence of V on α .

c. Semiempirical treatment of the strong interaction of levels: multi-level case. Eq. (7) can be easily generalized to a multi-level case as it simply gives the slope of a physical level a as a weighted average of the mixed levels. Thus, if the level a can be expressed as a linear combination of some unperturbed LS -states ψ_{L_n, S_n} :

$$|a\rangle = \sum_n C_n |\psi_{L_n, S_n}\rangle, \quad (8)$$

the resultant slope q_a is given by:

$$q_a = \sum_n C_n^2 q_n. \quad (9)$$

Here again we neglect weak dependence of interaction V on x in comparison to strong dependence of C_n^2 on x near crossing points.

Eq. (9) allows to improve *ab initio* coefficients q if we can find the expansion coefficients C_n in Eq. (8). That can be done, for example, by fitting g -factors. The magnetic moment operator $\boldsymbol{\mu} = g_0(\mathbf{L} + 2\mathbf{S})$ is diagonal in L and S and, therefore, does not mix different LS -states. Thus, in the LS -basis the resultant g -factor for the state a has exactly the same form as q_a :

$$g_a = \sum_n C_n^2 g_n. \quad (10)$$

If the experimental g -factors are known, one can use Eq. (10) to find weights C_n^2 and, then find the corrected values of the slopes q_a .

Sometimes, the experimental data on g -factors are incomplete. Then, one can still use a simplified version of Eqs. (9) and (10):

$$g_a = C^2 g_a^0 + (1 - C^2) \bar{g}, \Rightarrow C^2 = \frac{g_a - \bar{g}}{g_a^0 - \bar{g}}, \quad (11a)$$

$$q_a = C^2 q_a^0 + (1 - C^2) \bar{q}. \quad (11b)$$

C^2 here is the weight of the dominant LS -level in the experimental one, and the bar means the averaging over the admixing levels. Of course, there is some arbitrariness in calculation of averages \bar{g} and \bar{q} . However, the advantage of Eqs. (11) is that only one experimental g -factor is required.

III. DETAILS OF THE CALCULATION AND RESULTS

As we mentioned above, we performed calculations of energy levels for three values of the parameter x : $x_- = -1/8$, $x_0 = 0$, and $x_+ = 1/8$. All three calculations were done at exactly same level of approximation, to minimize the error caused by the incompleteness of the basis sets and configuration sets. From these calculations we found two approximations for q : $q_- = 8(\omega(x_0) - \omega(x_-))$ and $q_+ = 8(\omega(x_+) - \omega(x_0))$. If there were problems with level identification we performed additional calculation for $x = 0.01$, where the LS -coupling should be very accurate and identification is straightforward. The noticeable difference between q_- and q_+ signaled the possibility of the level crossing. In these cases we applied the semiempirical procedure described in Sec. II to find the corrected values for q ; otherwise, we simply took the average: $q = (q_+ + q_-)/2$.

A. Zn II

Zn II has the ground state configuration $[1s^2 \dots 3d^{10}]4s$ and we are interested in the $4s \rightarrow 4p_j$ transitions. As the theory here is much simpler than for other ions, we

TABLE II: Transition frequencies and parameters q for Zn II (in cm^{-1}). Calculations were done in four different approximations: Dirac-Hartree-Fock-Coulomb (DHFC), Dirac-Hartree-Fock-Coulomb-Breit (DHFCB), Brueckner-Coulomb (BC), and Brueckner-Coulomb-Breit (BCB).

Transition	Exper.	DHFC	DHFCB	BC	BCB
transition frequencies					
$4s_{1/2} \rightarrow 4p_{1/2}$	48481.077	44610.1	44608.1	48391.2	48389.4
$\rightarrow 4p_{3/2}$	49355.002	45346.9	45330.0	49263.8	49244.6
parameters $q = (q_+ + q_-)/2$					
$4s_{1/2} \rightarrow 4p_{1/2}$		1362	1359	1594	1590
$\rightarrow 4p_{3/2}$		2129	2109	2500	2479

used Zn II to study the importance of the core-valence correlation correction and Breit correction to the slopes q . The former correction was calculated in Brueckner approximation:

$$(H_{\text{DHF}} + \Sigma(E))\Psi = E\Psi, \quad (12)$$

with the self-energy operator $\Sigma(E)$ calculated in the second order of MBPT (the perturbation here is the difference between the exact and Dirac-Hartree-Fock Hamiltonians, $V = H - H_{\text{DHF}}$). The H_{DHF} was calculated with the magnetic part of the Breit operator included self-consistently. The retardation part of the Breit operator is known to be significantly smaller [29] and we completely neglected it here.

The results of our calculations of the frequencies ω and the slopes q for two transitions $4s \rightarrow 4p_j$, $j = 1/2, 3/2$ are given in Table II. One can see, that both Brueckner-Coulomb and Brueckner-Coulomb-Breit approximations give very good transition frequencies, accurate to 0.2%, though the latter slightly underestimates the fine splitting. Breit correction to the parameters q does not exceed 1%, while core-valence correlations account for the 17% correction.

In Table II we did not give separately the values of q_{\pm} . The difference between them is close to 1%. Indeed, in the absence of close interacting levels the dependence of q on x arise from the corrections to the energy of the order of $\alpha^4 Z^4$, which are very small.

B. Si II

Si II has three valence electrons and the ground state configuration $[1s^2 \dots 2p^6]3s^2 3p$. Excited configurations of interest are $3s3p^2$ and $3s^2 4s$. We made the CI calculation in the Coulomb approximation on the basis set, which included $1s - 8s$, $2p - 8p$, $3d - 8d$, and $4f$, $5f$ orbitals, which we denote as the basis set [8spd5f]. Note, that we use virtual orbitals, which are localized within the atom [34], rather than Dirac-Fock ones. This provides fast convergence. CI included all single-double (SD) and partly triple excitations from three valence configurations listed above. The results of these calculations are given in Table III.

TABLE III: Transition frequencies ω from the ground state ${}^2P_{1/2}^o$, fine structure splitting Δ_{FS} , and parameters q_{\pm} for Si II (in cm^{-1}).

	Experiment [35]		Theory			
	ω	Δ_{FS}	ω	Δ_{FS}	q_-	q_+
${}^2P_{3/2}^o$	287	287	293	293	295	291
${}^4P_{1/2}$	44080		41643		453	451
${}^4P_{3/2}$	44191	111	41754	111	565	564
${}^4P_{5/2}$	44364	174	41935	181	746	744
${}^2D_{3/2}$	55304		54655		509	507
${}^2D_{5/2}$	55320	16	54675	20	530	530
${}^2S_{1/2}$	65495		65148		40	39

Like in Zn, the left and right derivatives q_- and q_+ are close to each other, and all levels with equal exact quantum numbers are well separated. The astrophysical data exist for the levels ${}^2S_{1/2}$ and ${}^2D_{5/2}$. The former corresponds to the $3p \rightarrow 4s$ transition and has small slope q , while the latter corresponds to the $3s \rightarrow 3p$ transition and has much larger positive q . That is in agreement with the fact, that relativistic corrections to the energy usually decrease with the principle quantum number n and with the orbital quantum number l . Therefore, for the $ns \rightarrow np$ transition one should expect large and positive q , while for $np \rightarrow (n+1)s$, there should be large cancellation of relativistic corrections to upper and to lower levels, resulting in smaller q (see discussion in [25, 26]). The dominant correction to our results should be from the core-valence correlations. In the recent calculations of Mg, which has the same core as Si II, the core-valence corrections to transition frequencies were found to be about 4% [33, 36]. We conservatively estimate corresponding correction to q to be 6% of the larger q , i.e. 30 cm^{-1} .

C. Cr II

Cr II has the ground state configuration $[1s^2 \dots 3p^6]3d^5$ with five valence electrons. The astrophysical data correspond to the $3d \rightarrow 4p$ transition, for which one may expect negative value of q . CI calculations here are much more complicated, than for Si II. There is strong relaxation of the $3d$ shell in the discussed transition, which requires more basic d -orbitals. Therefore, we used the [6sp9d6f] basis set. In CI we included only single and double (SD) excitations. Some of the triple, quadruple, and octuple excitations were accounted for by means of the second order perturbation theory. It was found that corresponding corrections to transition frequencies were of the order of few percent, and were even smaller for parameters q . In general, these corrections did not improve the agreement with the experiment, so we present only CI results in Table IV.

As we mentioned above, there is strong relaxation of the $3d$ -shell in the $3d \rightarrow 4p$ transition. We were not able to saturate CI space and completely account for this

TABLE IV: Transition frequencies ω from the ground state ${}^6S_{5/2}$, fine structure splitting Δ_{FS} , and parameters q for Cr II (in cm^{-1}). CI single-double approximation was used for the Coulomb-Breit interaction.

	Experiment		Theory		
	ω	Δ_{FS}	ω	Δ_{FS}	q_+
${}^6D_{5/2}$	12148		13123		-2314
${}^6D_{7/2}$	12304	156	13289	165	-2153
${}^6F_{1/2}^o$	46824		47163		-1798
${}^6F_{3/2}^o$	46906	82	47244	81	-1715
${}^6F_{5/2}^o$	47041	135	47378	134	-1579
${}^6F_{7/2}^o$	47228	187	47565	187	-1387
${}^6F_{9/2}^o$	47465	237	47803	238	-1148
${}^6F_{11/2}^o$	47752	287	48091	288	-862
${}^6P_{1/2}^o$	48399		48684		-1364
${}^6P_{2/2}^o$	48491	92	48790	106	-1278
${}^6P_{3/2}^o$	48632	141	48947	157	-1108

relaxation. Because of that, we estimate the error for q here to be close to 10%.

We have seen before for Zn II and Si II, that in the absence of level-crossing the difference between q_+ and q_- is smaller than other theoretical uncertainties. In Cr II there are no close levels which may interact with each other, so in the calculation presented in Table IV we determined only the right derivative q_+ . In calculations with different basis sets we checked that the difference between q_+ and q_- is much smaller than the given above theoretical error (see Table I).

D. Fe II

Fe II ion has 7 valence electrons in configuration $3d^64s$ and represents the most complicated case. The astrophysical data includes 5 lines in the band 38000 cm^{-1} – 43000 cm^{-1} and two lines with the frequency close to 62000 cm^{-1} . The first band consists of three close, but separated multiplets with a regular fine structure splittings. The 62000 cm^{-1} band is completely different as the multiplets here strongly overlap and fine structure intervals are irregular [35]. Characteristic distance between the levels with identical exact quantum numbers is few hundred cm^{-1} , which is comparable to the fine structure splittings. This means that the levels strongly interact and even their identification may be a problem.

In fact, in Moore Tables [35] one of the multiplets of interest, namely y^6P^o , is erroneously assign to the configuration $3d^6({}^7S)4p$. It is an obvious misprint, as there is no term 7S for configuration $3d^6$. This term appears, however, in the configuration $3d^5$ and the correct assignment of this multiplet should be $3d^5({}^7S)4s4p$. This assignment is in agreement with our calculations and with the experimental g -factor of the level with $J = 7/2$. We checked that all close levels of the configuration $3d^64p$ have significantly smaller g -factors.

This reassignment has dramatic consequences in terms

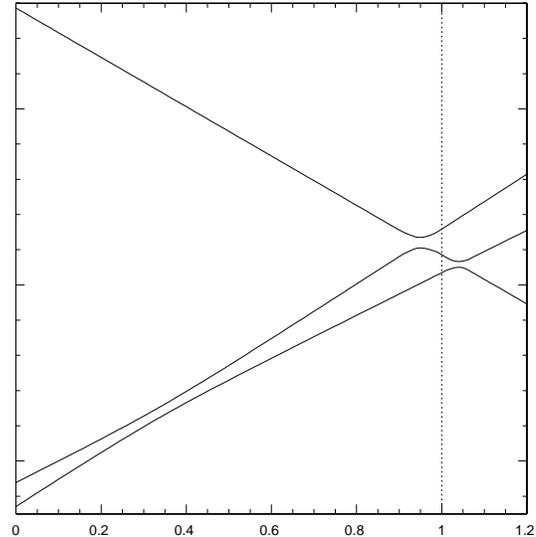


FIG. 1: Examples of typical interaction of levels in the upper band of Fe II. Levels are shown in arbitrary units as function of $(\alpha/\alpha_0)^2 = x + 1$. Levels of configuration $3d^6 4p$ have similar slopes and strongly interact with each other. That causes wide pseudo-crossings, similar to one shown on the left side of the plot. The level ${}^6P_{7/2}^o$ of the configuration $3d^5 4s 4p$ moves in the opposite direction. A series of sharp pseudo-crossings takes place near the physical value of α , marked by a vertical dotted line.

of the corresponding parameter q as configurations $3d^6 4p$ ($4s - 4p$ transition from the ground state) and $3d^5 4s 4p$ ($3d - 4p$ transition) move in the opposite directions from the ground state configuration $3d^6 4s$ when x is changed. It also causes a number of pseudo-crossings to occur right in the vicinity of $x = 0$ (see Fig. 1).

CI calculations for Fe II were done on the basis set [6spdf] in the SD approximation (see Table V). Triple excitations were included within second order perturbation theory and corresponding corrections were found to be relatively small. One can see from Table V that for the lower band both frequencies and g -factors are reproduced rather accurately.

The first anomaly takes place at 44000 cm^{-1} , where the levels ${}^4D_{7/2}^o$ and ${}^4F_{7/2}^o$ appear in the reverse order. Theoretical g -factors are also much further from LS values (1.429 and 1.238). That means that theoretical levels are at pseudo-crossing, while experimental levels already passed it. Indeed, calculations for $x = 1/8$ show that the right order of levels is restored, though the g -factors are still too far from LS values.

The second anomaly corresponds to the band above 60000 cm^{-1} . Here the order of calculated levels differs from that of the experimental ones. Note, that for this band only levels of negative parity with $J = 7/2$ are given in Table V. Thus, all of them can interact with each other. Let us estimate, how this interaction can

TABLE V: Transition frequencies ω from the ground state ${}^6D_{9/2}$, g -factors, and parameters q_{\pm} for Fe II (in cm^{-1}).

	Experiment		Theory				
	ω	g	ω	g	$g(LS)$	q_-	q_+
${}^6D_{9/2}^o$	38459	1.542	38352		1.556	1359	1363
${}^6D_{7/2}^o$	38660	1.584	38554	1.586	1.587	1522	1510
${}^6F_{11/2}^o$	41968		41864		1.455	1496	1508
${}^6F_{9/2}^o$	42115	1.43	42012		1.434	1615	1631
${}^6F_{7/2}^o$	42237	1.399	42141	1.396	1.397	1738	1737
${}^6P_{7/2}^o$	42658	1.702	42715	1.709	1.714	1241	1261
${}^4D_{7/2}^o$	44447	1.40	44600	1.345	1.429	1791	1837
${}^4F_{7/2}^o$	44754	1.29	44386	1.327	1.238	1608	1601
${}^8P_{7/2}^o$	54490		54914	1.936	1.937	-2084	-2086
${}^4G_{7/2}^o$	60957	0.969	63624	0.978	0.984	1640	1640
${}^4H_{7/2}^o$	61157	0.720	63498	0.703	0.667	1296	1247
${}^4D_{7/2}^o$	61726	1.411	66145	1.398	1.429	1194	1240
${}^4F_{7/2}^o$	62066	1.198	65528	1.252	1.238	1071	1052
${}^6P_{7/2}^o$	62172	1.68	65750	1.713	1.714	-1524	-1514
${}^2G_{7/2}^o$	62323		64798	0.882	0.889	1622	1605

affect the slopes q .

Five levels from this band belong to configuration $3d^64p$ and have close slopes with the average $\bar{q} = 1360 \text{ cm}^{-1}$. Only the level ${}^4F_{7/2}^o$ has the slope, which is 300 cm^{-1} smaller, than the average. The remaining level ${}^6P_{7/2}^o$ belongs to configuration $3d^54s4p$ and has the slope of the opposite sign $q_1 = -1519 \text{ cm}^{-1}$. Its absolute value is 500 cm^{-1} smaller, than for the level ${}^8P_{7/2}^o$ of the same configuration $3d^54s4p$. That suggests that the levels ${}^4F_{7/2}^o$ and ${}^6P_{7/2}^o$ strongly interact with each other. This is also in agreement with the fact, that these levels are the closest neighbors both experimentally and theoretically and that they cross somewhere between x_- and x . There is also strong interaction between the levels ${}^2G_{7/2}^o$, ${}^4F_{7/2}^o$, and ${}^4D_{7/2}^o$. That can be seen if one calculates the scalar products (overlaps) between corresponding wave functions for different values of x , such as: $\langle i(x_-)|k(x_+)\rangle$. For weakly interacting levels $\langle i(x_-)|k(x_0)\rangle \approx \langle i(x_-)|k(x_+)\rangle \approx \delta_{i,k}$, so large non-diagonal matrix elements signal, that corresponding levels interact.

Interaction of levels ${}^2G_{7/2}^o$, ${}^4F_{7/2}^o$, and ${}^4D_{7/2}^o$ does not affect the slopes q as strongly, as the interaction of ${}^4F_{7/2}^o$ and ${}^6P_{7/2}^o$, so we can account for the former in a less accurate way, but it is important to include the latter as accurately as possible.

The level ${}^6P_{7/2}^o$ interacts with some linear combination of levels ${}^2G_{7/2}^o$, ${}^4F_{7/2}^o$, and ${}^4D_{7/2}^o$. The slopes and g -factors of the latter are relatively close to each other, so we can simply take the average for all three:

$$\bar{g} = 1.185; \quad \bar{q} = 1297. \quad (13)$$

Now we can use experimental g -factor of the state ${}^6P_{7/2}^o$

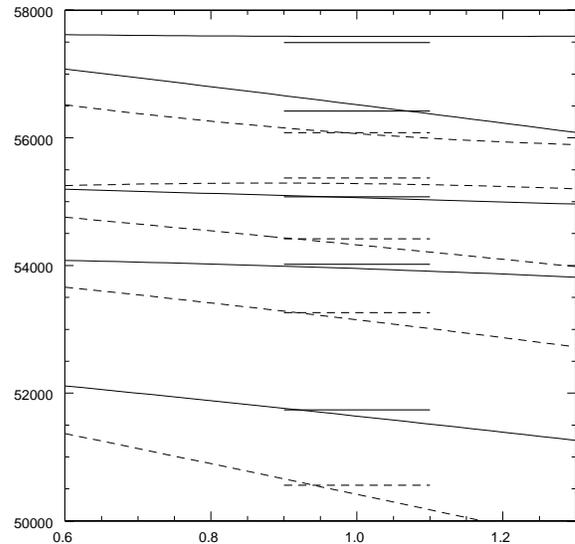


FIG. 2: Dependence of the odd levels of Ni II on $(\alpha/\alpha_0)^2 = x + 1$. Solid lines correspond to $J = 5/2$ and dashed lines to $J = 7/2$. The experimental positions of the lines are shown as short horizontal lines and are all shifted by 1000 cm^{-1} . The order of levels from bottom up: ${}^4D_{7/2,5/2}^o$, ${}^4G_{7/2,5/2}^o$, ${}^4F_{7/2,5/2}^o$, ${}^2G_{7/2}^o$, ${}^2F_{5/2}^o$, ${}^2D_{5/2}^o$, and ${}^2F_{5/2}^o$.

and Eq. (11) to determine the mixing:

$$C^2 = \frac{1.68 - \bar{g}}{1.713 - \bar{g}} = 0.937, \quad (14)$$

$$q({}^6P_{7/2}^o) = -1342. \quad (15)$$

Eq. (15) corresponds to the correction $\delta\bar{q} = +177$. Therefore, for the closest level ${}^4F_{7/2}^o$ this model gives an estimate:

$$q({}^4F_{7/2}^o) = \bar{q} - \delta\bar{q} = 1120. \quad (16)$$

Eqs. (15) and (16) show that correction for the mixing is not very large. That corresponds to the fact that experimental g -factor of the level ${}^6P_{7/2}^o$ is significantly larger than any g -factors of the levels of the configuration $3d^64p$. Thus, the interaction for this level is relatively small. On the contrary, the levels of the configuration $3d^64p$ strongly interact with each other, but corresponding changes of the slopes are also relatively small (since the q values for these strongly interacting levels are approximately the same).

We estimate the accuracy of our calculations for the lower band of Fe II to be about 150 cm^{-1} , and approximately 300 cm^{-1} for the values (15) and (16).

E. Ni II

Ni II has the ground state configuration $3d^9$. The spectrum is somewhat simpler, than for Fe II. There are also

TABLE VI: Transition frequencies ω from the ground state $^2D_{5/2}$, g -factors, and parameters q_{\pm} for Ni II (in cm^{-1}).

	Experiment		Theory				
	ω	g	ω	g	$g(LS)$	q_{-}	q_{+}
$^2D_{3/2}$	1507		1579		0.800	1559	1552
$^4D_{7/2}^o$	51558	1.420	50415	1.423	1.429	-2405	-2425
$^4D_{5/2}^o$	52739	1.356	51640	1.360	1.371	-1217	-1245
$^4G_{7/2}^o$	54263	1.02	53150	1.016	0.984	-1334	-1387
$^4G_{5/2}^o$	55019	0.616	53953	0.617	0.571	-370	-418
$^4F_{7/2}^o$	55418	1.184	54323	1.183	1.238	-1104	-1124
$^4F_{5/2}^o$	56075	0.985	55063	0.986	1.029	-332	-334
$^2G_{7/2}^o$	56372	0.940	55284	0.933	0.889	-60	-188
$^2F_{7/2}^o$	57080	1.154	56067	1.128	1.143	-911	-713
$^2D_{5/2}^o$	57420	1.116	56520	1.108	1.200	-1419	-1438
$^2F_{5/2}^o$	58493	0.946	57589	0.959	0.857	-35	-5

pseudo-crossings here, but they either lie far from $x = 0$, or are rather wide. That makes their treatment slightly easier. Nevertheless, our results significantly differ from previous calculations [28].

CI calculations were done for the Coulomb potential and included SD and partly triple excitations on the basis set [5spdf]. We calculated 5 lower odd levels with $J = 5/2$ and 5 with $J = 7/2$ for x_{-} , x_0 , and x_{+} , and used parabolic extrapolation for the interval $-0.4 \leq x \leq +0.3$ (see Fig. 2). It is seen that the theory accurately reproduce relative positions of all levels. An overall agreement between the theory and the experiment becomes close to perfect if all experimental levels are shifted by 1000 cm^{-1} down, as it is done in Fig. 2. Note, that this shift constitutes only 2% of the average transition frequency.

Calculated g -factors are generally in agreement with the experiment [35] and noticeably different from the pure LS -values (see Table VI). However, for the level $^2F_{7/2}^o$ theoretical g -factor is smaller than the LS value, while experimental one is larger. There are no nearby levels who may mix to this one and move g -factor closer to experiment. On the other hand, the difference with experiment is only 2% and may be within experimental accuracy.

Fig. 2 shows that the levels $^2G_{7/2}^o$ and $^2F_{7/2}^o$ cross at $x \approx 0.3$ and they already strongly interact at $x = 0$. Theoretical splitting for these levels is 10% larger than experimental one. Thus, they are in fact even closer to the crossing point than is predicted by the theory. The experimental splitting is equal to the theoretical one for larger value of α corresponding to $x \approx 0.15$. At $x = 0.15$ the slopes of these levels are -265 and -590 , and for $x = 0$ they are -124 and -812 correspondingly. Note, that the sum of the slopes at $x = 0.15$ differs by 80 cm^{-1} from the sum at $x = 0$. According to Eq. (7) for a two-level system the sum is constant. This means that these two levels repel from the lower lying level $^4F_{7/2}^o$. Taking this analysis into account we suggest an average between $x = 0$ and $x = 0.15$ as our final value: $q(^2F_{7/2}^o) = -700(250)$.

Conclusions

In this paper we present new refined calculations of the parameters q , which determine α -dependence of the transition frequencies for a number of ions used in the astrophysical search for α -variation. These ions appear to be very different from the theoretical point of view. Because of that we had to use different methods and different levels of approximation for them. The final accuracy of our results differs not only for different ions, but also for different transitions.

The simplest system is Zn II, which has one valence electron. On the other hand, this is the heaviest ion and it has the largest core, which includes $3d^{10}$ -shell. That gave us the opportunity to study corrections to q from the core-valence correlations and from Breit interaction. We found the former to be about 17% and the latter to be less than 1%. For lighter ions Breit interaction should be even smaller and can be safely neglected. Other ions also have much smaller and more rigid cores, so one might expect that core-valence correlations are few times weaker there in comparison to Zn. That allows us to neglect core-valence correlations for all other ions discussed in this paper.

Si II has the smallest core $1s^2 \dots 2p^6$ and three valence electrons. For neutral Mg, which has the same core, the core-valence corrections to the $3s \rightarrow 3p$ transition frequencies were found to be about 4% [33, 36]. CI calculation for Si II is relatively simple and the errors associated with incompleteness of CI space are small. Thus, our estimate of the accuracy for Si on 6% level seems to be rather conservative.

Cr, Fe, and Ni have the core $1s^2 \dots 3p^6$ and the core excitation energy varies from 2 a.u. for Cr II to 2.6 a.u. for Ni II. In comparison, the core excitation energy for Zn II is 0.9 a.u. Therefore, we estimate the core-valence correlation corrections for these ions to be at least two times smaller, than for Zn II.

Additional error here is associated with incompleteness of the CI space. These ions have from 5 to 9 valence electrons and CI space can not be saturated. To estimate corresponding uncertainty we performed several calculations for each ion using different basis sets and two different computer packages described in Sec. II. The basic Dirac-Hartree-Fock orbitals were calculated for different configurations (for example, for the ground state configuration and for excited state configuration, etc.).

Supplementary information on the accuracy of our calculations can be obtained from comparison of calculated spectra and g -factors with experimental values. The later appear to be very important as they give information about electron coupling, which depends on relativistic corrections and on interaction between LS -multiplets. Our results for Cr II appear to be very close for different calculations and are in good agreement with the experiment both in terms of the gross level structure and spin-orbit splittings (see Table IV), so we estimate our final error here to be about 10 – 12%.

The largest theoretical uncertainties appear for Fe II and Ni II where the number of valence electrons is largest and the interaction of levels is strongest. Here we had to include semi-empirical fits to improve the agreement between the theory and the experiment. We took into account the size of these semi-empirical corrections in estimates of the accuracy of the calculated values of q .

The final results are presented in Table I. Note again, that they are based on several independent calculations performed using two different computer codes. Some of

the intermediate results are given in Table II – Table VI.

Acknowledgments

This work is supported by Australian Research Council. One of us (MK) thanks UNSW for hospitality and acknowledges support from the Gordon Godfrey Fund.

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