

# $\alpha$ dependence of transition frequencies for ions Si II, Cr II, Fe II, Ni II, and Zn II

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We perform an improved calculation of the  $\alpha$  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  $\alpha$  in space-time. We use the Dirac-Hartree-Fock method as a zero approximation and then the many-body perturbation theory and configuration-interaction methods to improve the results. The important problem of level pseudocrossing (as a function of  $\alpha$ ) is considered. Near the crossing point the derivative of the frequency over  $\alpha$  varies strongly (including a change of sign). This makes it very sensitive to the position of the crossing point. We propose a semiempirical solution of the problem, which allows us to obtain accurate results.

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## 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 of such variation was reported in [1–6] from analysis of 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., [7–9]) and from precision laboratory measurements [10–12]. Recently, a number of other laboratory tests have been proposed (see, e.g., [13]). The analysis of the microwave background radiation can also give some restrictions on the time variation of  $\alpha$  as suggested in [14–16]. Implementations of the space-time variation of the fine-structure constant in the theory of fundamental interactions are discussed, e.g., in Refs. [17–23] (see also the discussion and references in [3]).

The most straightforward way to look for the variation of  $\alpha$  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  $\omega(n's_{1/2} \rightarrow np_{3/2})$ .<sup>1</sup> 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 easily be converted into the space-time variation of  $\alpha$ . However, as was pointed out in [25], one can gain about an order of magnitude in the sensitivity to the  $\alpha$  variation by comparing optical transitions for different atoms. In this case the frequency of each transition can be expanded in a series in  $\alpha^2$ :

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

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

where  $\alpha_0$  stands for the laboratory value of the fine-structure 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 Eq. (1a) turns out to be zero, while for 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 the corresponding coefficients for 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]). Consequently, the ratio (3) is, in general, more sensitive to the variation of  $\alpha$  than the ratio (2). It is also important that the signs of the coefficients  $\omega_i^{(2)}$  in Eq. (3) can vary. For example, for  $s$ - $p$  transitions the relativistic corrections are positive while for  $d$ - $p$  transitions they are negative. This allows us to suppress possible systematic errors that are independent of 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 multielectron atom, where the spectrum is very dense. And this happens to be a typical situation for astrophysical spectra, in particular, for large cosmological redshifts. Corresponding atomic calculations have to account very accurately for the electronic correlations, which may affect such spectra quite dramatically.

Earlier calculations of the coefficients  $q$  from Eq. (1) for transitions suitable for astronomical and laboratory measurements were done in Refs. [25–28]. Here we present improved calculations of the coefficients  $q$  for the transitions,

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<sup>1</sup>In fact, the frequency  $\omega(np_{1/2} \rightarrow np_{3/2})$  is not measured directly, but is found as a difference:  $\omega(n's_{1/2} \rightarrow np_{3/2}) - \omega(n's_{1/2} \rightarrow np_{1/2})$ .

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 parentheses. Results of the previous calculations [3] are given for comparison.

Ion	Transition	$\omega_0$ (cm <sup>-1</sup> )	$q$ (cm <sup>-1</sup> )		
			This work	[3]	
Si II	$^2P_{1/2}^o \rightarrow ^2D_{3/2}$	55309.337	520	(30)	530
	$\rightarrow ^2S_{1/2}$	65500.449	50	(30)	70
Cr II	$^6S_{5/2} \rightarrow ^6P_{3/2}^o$	48398.868	-1360	(150)	-1290
	$\rightarrow ^6P_{5/2}^o$	48491.053	-1280	(150)	-1200
	$\rightarrow ^6P_{7/2}^o$	48632.055	-1110	(150)	-1060
Fe II	$^6D_{9/2} \rightarrow ^6D_{9/2}^o$	38458.987	1330	(150)	1450
	$\rightarrow ^6D_{7/2}^o$	38660.049	1490	(150)	1620
	$\rightarrow ^6F_{11/2}^o$	41968.064	1460	(150)	1640
	$\rightarrow ^6F_{9/2}^o$	42114.833	1590	(150)	1780
	$\rightarrow ^6P_{7/2}^o$	42658.240	1210	(150)	1420
	$\rightarrow ^4F_{7/2}^o$	62065.528	1100	(300)	1210
	$\rightarrow ^6P_{7/2}^o$	62171.625	-1300	(300)	1280
	$\rightarrow ^2D_{5/2}$	57080.373	-700	(250)	-300
Ni II	$\rightarrow ^2D_{5/2}^o$	57420.013	-1400	(250)	-700
	$\rightarrow ^2F_{5/2}^o$	58493.071	-20	(250)	800
	$\rightarrow ^2P_{1/2}^o$	48481.077	1584	(25)	1577
Zn II	$\rightarrow ^2P_{3/2}^o$	49355.002	2490	(25)	2479

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 simplest atoms Mg and Al, where the previous calculation [25] should be sufficiently accurate; we focus 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 earlier works, and  $q \equiv \partial\omega/\partial x|_{x=0} = q_1 + 2q_2$ .

For comparison, in the last column of Table I we present the results of the previous calculations [25,26,28] (the results were summarized in Ref. [3], which also contains some original calculations). The improved calculations in the present work agree with the old results for the majority of the transitions. However, there are several important exceptions. The coefficient  $q$  for the 62 172 cm<sup>-1</sup> transition in Fe II has changed its sign. This is because the excited level in this transition was incorrectly identified (in [35] it was erroneously assigned to the configuration  $3d^64p$ ). There are also significant changes to the Ni II transitions. In [28] the accuracy in the *ab initio* calculations of the energy levels and  $g$  factors was not high. In the present work we have radically improved this accuracy. To increase our confidence in the final results, we have performed calculations using two different computer codes, which give close values for  $q$ . Therefore, we believe that our values are more accurate and reliable than the old ones.

Details of the calculations and discussion of the accuracy is given below in Sec. III. Before that we briefly address a few theoretical points in Sec. II.

## II. THEORY

In order to find the 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 to estimate the second derivative  $\partial^2\omega/\partial x^2|_{x=0}$ . A 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 multielectron 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. Although 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. In the next step the core-valence correlations can be accounted for by means of many-body perturbation theory (MBPT). Already the second order MBPT correction allows us to reproduce the spectrum with 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 the configuration-interaction (CI) method. If necessary, the core-valence correlations can be included within a combined CI + MBPT technique [30]. This 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 [30–32]. However, the accuracy of *ab initio* methods decreases with increasing 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 levels with the same exact quantum numbers strongly interact with each other. The part of the spectrum of Fe II above 55 000 cm<sup>-1</sup> and, to a somewhat lesser extent, the spectrum of Ni II represent this situation. Accordingly, 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 method we performed calculations for most of the ions with two different computer packages. One package was used earlier in Refs. [30,32,33] and the other was used in Refs. [3,25–28,31]. The former package allows one 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 an atom  $J$ . When there were no significant differences 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: Pseudocrossing**

In the nonrelativistic limit  $\alpha \rightarrow 0$ , all multielectron 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  $n$  enumerates levels with the same  $p, L, S$ , and  $J$ . For sufficiently small values of  $\alpha$  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 large parentheses gives the slope for the center of the multiplet, and the second term gives the fine structure. With growing  $\alpha$  the multiplets start to overlap, and when levels with the same  $p$  and  $J$  come close, pseudocrossing takes place.

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

Let us first analyze the behavior of the slopes  $q(x)$  in the vicinity of the pseudocrossing 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

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

It is easy now to calculate the energy derivative with respect to  $x$  in terms of the mixing angle  $\phi$  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  $\phi$  varies from 0 on one side, through  $\pi/4$  in the center, to  $\pi/2$  on the other side, which leads to a change of 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  $\Delta x \approx V/|q_1 - q_2|$ . Thus, 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 the nondiagonal 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  $\alpha$ .

**C. Semiempirical treatment of the strong interaction of levels: Multilevel case**

Equation (7) can easily be generalized to a multilevel 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  $\psi_{L_n, S_n}$ ,

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

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 the interaction  $V$  on  $x$  in comparison to the strong dependence of  $C_n^2$  on  $x$  near crossing points.

Equation (9) allows us to improve the *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, for this reason, does not mix different  $LS$  states. Consequently, 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 the 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):

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

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

Here  $C^2$  is the weight of the dominant  $LS$  level in the experimental data, and the overbar means averaging over the mixing levels. Of course, there is some arbitrariness in the calculation of the 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 the exact 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  $q_+$

TABLE II. Transition frequencies and parameters  $q$  for Zn II (in  $\text{cm}^{-1}$ ). 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	Expt.	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

$=8[\omega(x_+) - \omega(x_0)]$ . If there were problems with level identification we performed additional calculations for  $x=0.01$ , where the  $LS$  coupling should be adequate, and identification is straightforward. The noticeable difference between  $q_-$  and  $q_+$  signaled the possibility of a 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 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 the 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 the Dirac-Hartree-Fock Hamiltonians,  $V = H - H_{\text{DHF}}$ ). The  $H_{\text{DHF}}$  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  $\omega$  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%, although 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 do 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  $x$  arises from 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 in-

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

	Expt. [35]		Theory			
	$\omega$	$\Delta_{\text{FS}}$	$\omega$	$\Delta_{\text{FS}}$	$q_-$	$q_+$
${}^2P_{3/2}^o$	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

terest are  $3s3p^2$  and  $3s^2 4s$ . We made a CI calculation in the Coulomb approximation on a basis set that included  $1s-8s$ ,  $2p-8p$ ,  $3d-8d$ , and  $4f, 5f$  orbitals (we denote it as the basis set  $[8spd5f]$ ). Note that we used virtual orbitals, which were localized within the atom [34], rather than Dirac-Fock ones. This provided 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.

As in Zn, the left and right derivatives  $q_-$  and  $q_+$  are close to each other, and all levels with exactly equal quantum numbers are well separated. 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 a much larger positive  $q$ . That is in agreement with the fact that relativistic corrections to the energy usually decrease with increasing principal quantum number  $n$  and increasing orbital quantum number  $l$ . Consequently, 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 the upper and lower levels, resulting in smaller  $q$  (see the discussion in [25,26]). The dominant correction to our results should be from the core-valence correlations. In the recent calculations for 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 the corresponding correction to  $q$  to be 6% of the larger  $q$ , i.e.,  $30 \text{ cm}^{-1}$ .

### 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 a 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 the CI we included only SD excitations. Some of the triple, quadruple, and octuple excitations were accounted for by means of second order perturbation theory. It was found that corresponding corrections to transition frequencies were of the order of a few percent, and were even smaller for the

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

	Experiment		Theory		
	$\omega$	$\Delta_{\text{FS}}$	$\omega$	$\Delta_{\text{FS}}$	$q_+$
${}^6D_{5/2}$	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
${}^6P_{3/2}^o$	48399		48684		-1364
${}^6P_{5/2}^o$	48491	92	48790	106	-1278
${}^6P_{7/2}^o$	48632	141	48947	157	-1108

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 was 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 effect. Because of that, we estimated 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 that 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 value of the given above theoretical error (see Table I).

#### D. Fe II

The Fe II ion has seven valence electrons in the configuration  $3d^64s$  and represents the most complicated case. The astrophysical data include five lines in the band  $38\,000\text{ cm}^{-1}$ – $43\,000\text{ cm}^{-1}$  and two lines with frequency close to  $62\,000\text{ cm}^{-1}$ . The first band consists of three close but separated multiplets with regular fine-structure splittings. The  $62\,000\text{ cm}^{-1}$  band is completely different, as the multiplets here strongly overlap and fine-structure intervals are irregular [35]. The characteristic distance between levels with identical exact quantum numbers is a few hundred  $\text{cm}^{-1}$ , which is comparable to the fine-structure splittings. That means that the levels strongly interact, and even their identification may be a problem.

In fact, in [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 the 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

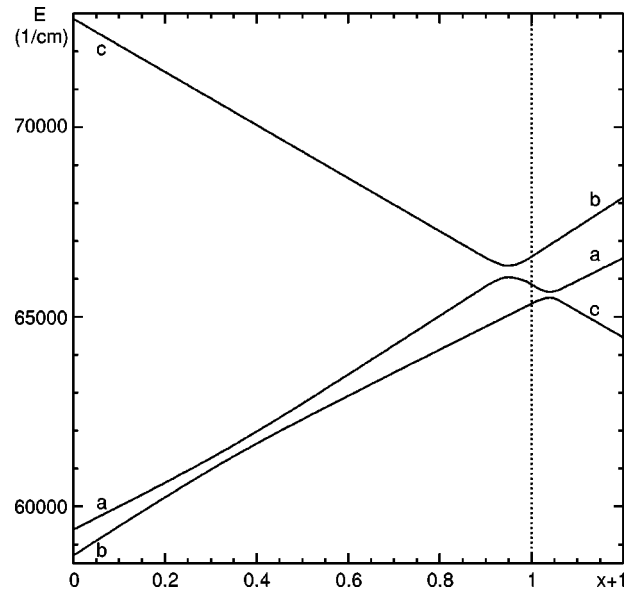


FIG. 1. Example of the typical interaction of levels in the upper band of Fe II. Levels are shown as functions of  $(\alpha/\alpha_0)^2 = x + 1$ . Levels of the configuration  $3d^64p$  have similar slopes and strongly interact with each other. That causes wide pseudocrossings, similar to the one between  ${}^4F_{7/2}^o(a)$  and  ${}^4D_{7/2}^o(b)$  shown on the left side of the plot. The level  ${}^6P_{7/2}^o(c)$  of the configuration  $3d^54s4p$  moves in the opposite direction. A series of sharp pseudocrossings takes place near the physical value of  $\alpha$ , marked by a vertical dotted line.

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 of the corresponding parameter  $q$ , as the configurations  $3d^64p$  ( $4s$ - $4p$  transition from the ground state) and  $3d^54s4p$  ( $3d$ - $4p$  transition) move in the opposite directions from the ground state configuration  $3d^64s$  when  $x$  is changed. It also causes a number of pseudocrossings 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  $44\,000\text{ cm}^{-1}$ , 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 the theoretical levels are at a pseudocrossing, while the experimental ones already passed it. Indeed, calculations for  $x = 1/8$  show that the right order of levels is restored, although the  $g$  factors are still too far from  $LS$  values.

The second anomaly corresponds to the band above  $60\,000\text{ cm}^{-1}$ . Here the order of the 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. Accordingly, all of them can interact with each other.

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

	Experiment		Theory				
	$\omega$	$g$	$\omega$	$g$	$g(LS)$	$q_-$	$q_+$
${}^6D_{9/2}$	38459	1.542	38352		1.556	1359	1363
${}^6D_{7/2}$	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
${}^4D_{9/2}^o$	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

Let us estimate how this interaction can affect the slopes  $q$ . Five levels from this band belong to the configuration  $3d^64p$  and have close slopes with the average  $\bar{q} = 1360 \text{ cm}^{-1}$ . Only the level  ${}^4F_{7/2}^o$  has a slope, that is  $300 \text{ cm}^{-1}$  smaller than the average. The remaining level  ${}^6P_{7/2}^o$  belongs to the configuration  $3d^54s4p$  and has a slope of the opposite sign  $q = -1519 \text{ cm}^{-1}$ . Its absolute value is  $500 \text{ cm}^{-1}$  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 nondiagonal 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 the experimental  $g$  factor of the state  ${}^6P_{7/2}^o$  and Eq. (11) to determine the mixing:

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

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

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

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

Equations (15) and (16) show that correction for the mixing is not very large. That corresponds to the fact that the 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  $150 \text{ cm}^{-1}$ , and approximately  $300 \text{ cm}^{-1}$  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 pseudocrossings 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 the five lowest odd levels with  $J=5/2$  and five levels 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 reproduces the relative positions of all levels. The overall agreement between the theory and the experiment becomes close to perfect, if all experimental levels are shifted down, by  $1000 \text{ cm}^{-1}$  as is done in Fig. 2. Note that this shift constitutes only 2% of the average transition frequency.

The 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  ${}^2F_{7/2}^o$  the theoretical  $g$  factor is smaller than the  $LS$  value, while the experimental one is larger. There are no nearby levels that may mix with this one and move the  $g$  factor closer to experiment. On the other hand, the difference from the experiment is only 2% and may be within experimental accuracy.

Figure 2 shows that the levels  ${}^2G_{7/2}^o(g)$  and  ${}^2F_{7/2}^o(h)$  cross at  $x \approx 0.3$ , and they already strongly interact at  $x=0$ . The theoretical splitting for these levels is 10% larger than the experimental one. Consequently, they are in fact even closer to the crossing point than is predicted by the theory.

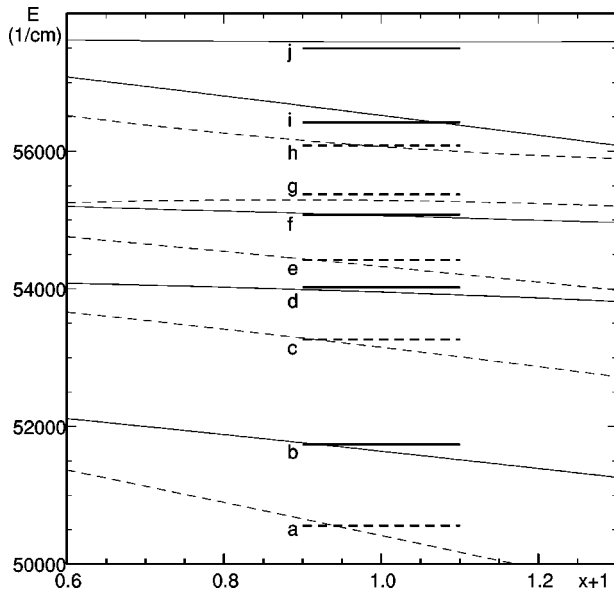


FIG. 2. Dependence of the odd levels of Ni II on  $(\alpha/\alpha_0)^2 = x + 1$ . Solid lines correspond to  $J=5/2$  and dashed lines to  $J=7/2$ . The experimental positions of the lines are shown as short horizontal lines and are all shifted down by  $1000 \text{ cm}^{-1}$ . The assignment of the levels from bottom up:  ${}^4D_{7/2,5/2}(a,b)$ ,  ${}^4G_{7/2,5/2}(c,d)$ ,  ${}^4F_{7/2,5/2}(e,f)$ ,  ${}^2G_{7/2}(g)$ ,  ${}^2F_{7/2}(h)$ ,  ${}^2D_{5/2}(i)$ , and  ${}^2F_{5/2}(j)$ .

The experimental splitting is equal to the theoretical one for larger value of  $\alpha$  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  $-812$ , respectively. Note that the sum of the slopes at  $x=0.15$  differs by  $80 \text{ cm}^{-1}$  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 are repelled from the lower-lying level  ${}^4F_{7/2}(e)$ . Taking this analysis into account, we suggest an average between  $x=0$  and  $x=0.15$  as our final value:  $q({}^2F_{7/2}^o) = -700(250)$ .

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

	Experiment		Theory				
	$\omega$	$g$	$\omega$	$g$	$g(LS)$	$q_-$	$q_+$
${}^2D_{3/2}$	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

#### IV. CONCLUSIONS

In this paper we present refined calculations of the parameters  $q$ , which determine the  $\alpha$  dependence of the transition frequencies for a number of ions used in the astrophysical search for  $\alpha$  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 a  $3d^{10}$  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 the 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 a 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]. The 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 the incompleteness of the CI space. These ions have from five to nine valence electrons and the CI space cannot be saturated. To estimate the 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 the 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 latter 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 in terms of both 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 semiempirical fits to improve the agreement between the theory and the experiment. We took into account the size of

these semiempirical 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 Tables II–VI.

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