

Transition frequency shifts with fine-structure constant variation for Fe I and isotope-shift calculations in Fe I and Fe II

S. G. Porsev,^{1,2} M. G. Kozlov,^{1,2} and D. Reimers²¹*Petersburg Nuclear Physics Institute, Leningrad district, Gatchina, 188300, Russia*²*Hamburger Sternwarte, Universität Hamburg, Hamburg 21029, Germany*

(Received 15 December 2008; published 31 March 2009)

In this paper we calculated the relativistic corrections to transition frequencies (q factors) of Fe I for the transitions from the even- and odd-parity states to the ground state. We also carried out isotope-shift calculations in Fe I and Fe II.

DOI: [10.1103/PhysRevA.79.032519](https://doi.org/10.1103/PhysRevA.79.032519)

PACS number(s): 31.30.Gs, 06.20.Jr, 31.15.am

I. INTRODUCTION

The problem of temporal and spatial variation of the fundamental physical constants is actively discussed in the literature during last several years. A recent review of its current status can be found elsewhere [1]. One of the reasons stimulating this activity was the discovery of acceleration of the universe (for a review see [2]), what is usually associated with the existence of the dark energy. Modern theories describing cosmological evolution predict that the dark energy may cause variations of the fundamental constants.

A statement that the fine-structure (FS) constant α was possibly changed during evolution of the universe was made by Australian group in Ref. [3]. Other astrophysical groups do not confirm this result [4,5], and hence new laboratory and astrophysical investigations are required.

Laboratory studies of hypothetical variation of the fine-structure constant are based on the fact that transition frequencies in atoms depend on αZ , where Z is atomic number. Supposing that the nowadays value of α differs from its value in the earlier universe we can study space-time variation of α by comparing atomic frequencies for distant objects in the universe with their laboratory values. In practice, we need to find relativistic frequencies shifts, determined by so-called q factors, according to

$$\omega = \omega_{\text{lab}} + qx, \quad x \equiv (\alpha/\alpha_{\text{lab}})^2 - 1. \quad (1)$$

Most advantageous for these studies are the atoms and ions for which q factors of transitions between certain states significantly differ from each other. At the same time these elements should be abundant in the universe to provide sufficient observable data. Fe I and Fe II discussed in this paper meet both these conditions. Spectra of Fe II were used by several groups [3–5] within “many-multiplet method” and by Levshakov *et al.* within “single-ion differential alpha measurement method” [6]. The atoms of Fe I were observed in resonance ultraviolet lines in two damped Ly α systems at $z=0.452$ [7] and $z=1.15$ [8]. According to [9] the spectra of Fe I are also observed for the high redshift quasars and may be used for the α -variation search. In this work we calculate the q factors for the transitions in Fe I from the even- and odd-parity states to the ground state.

As was pointed out in many papers including [3,10–13] one of the problems that occurs in the study of possible α variation is a necessity to separate this effect from the

isotope-shift (IS) effect. A method to resolve this problem was suggested in [12]. This method requires (along with a knowledge of atomic relativistic coefficients q) an accurate knowledge of the isotope-shift coefficients.

In this paper we carry out isotope-shift calculations in Fe I and Fe II. We compare the results obtained for Fe II with other available theoretical data. Experimental study of the IS in ultraviolet transitions in Fe II is rather difficult. A method for such experiments has been recently suggested in [14].

The paper is organized as follows. Sec. II is devoted to the method of calculation of the properties of Fe I. We discuss the results obtained for the q factors. In Sec. III the method of calculation of isotope shift is described. We present the results of the isotope-shift calculation in Fe I and Fe II. Finally, Sec. IV contains concluding remarks. Atomic units ($\hbar=|e|=m_e=1$) are used throughout the paper.

II. CALCULATION OF q FACTORS FOR Fe I

A. Method of calculation

To find q factors we need to solve the atomic relativistic eigenvalue problem for different values of α or, respectively, for different values of x from Eq. (1). We can calculate atomic frequencies ω_{\pm} for two values $x=\pm 1/8$ of the parameter x . Our experience shows that such a choice of x allows us to meet two conditions. The value $|x|=1/8$ is usually sufficiently small to neglect nonlinear corrections and sufficiently large to make calculations numerically stable. The corresponding q factor is given by

$$q = 4(\omega_+ - \omega_-). \quad (2)$$

The ground-state configuration of Fe I is $(1s^2-3d^64s^2)$. Since it has eight electrons in open shells its spectrum is rather dense and complicated. Due to proximity of the levels with the same total angular momentum (especially in the middle of spectrum which astrophysically is most interesting) they strongly interact with each other. All this makes calculations of Fe I very difficult. A calculation of q factors for neutral iron was carried out recently by Dzuba and Flambaum in Ref. [15]. They used a simple method combining *ab initio* Hartree-Fock and configuration-interaction (CI) technique with some semiempirical fitting of energy levels.

In this paper we make pure *ab initio* calculations in the frame of the eight-electron CI method. The $[1s^2-3p^6]$ elec-

trons are treated as core electrons while $3d$, $4s$, and $4p$ electrons are in the valence space. The number of configurations accounted for in our calculations is noticeably greater than in [15]. As a result an effect of configuration interaction is treated more accurately. Below we will discuss it in more detail.

We started from solving the Dirac-Hartree-Fock (DHF) equations. The self-consistency procedure was done for $(1s^2-3d^64s^2)$ configuration. After that the $4p_{1/2}$ and $4p_{3/2}$ orbitals were constructed as follows. All electrons were frozen; one electron from the $4s$ shell was moved to the $3d$ shell and another electron from the $4s$ shell was moved to $4p$ shell. Thus, the valence orbitals $4p_{1/2}$ and $4p_{3/2}$ were constructed for the $3d^74p$ configuration.

On the next stage we constructed virtual orbitals. We used the method described in [16,17] and applied by us for calculating different properties of Fe II [18]. In this method an upper component of virtual orbitals is formed from the previous orbital of the same symmetry by multiplication by some smooth function of radial variable r . The lower component is then formed using kinetic balance condition.

Our basis sets included s , p , d , and f orbitals with principle quantum number $n \leq N$. We designate them as $[Nspdf]$. We have carried out the calculations of energy levels, g , and q factors for three basis sets with $N=4-6$. Configuration space was formed by single and double (SD) excitations from the configurations $3d^64s^2$, $3d^64s4p$, and $3d^74p$.

Additionally we studied Breit corrections including the Breit interaction into consideration. For $4spdf$ basis set we computed q factors in the Coulomb-Breit approximation and compared them with the results obtained in pure Coulomb approximation. As analysis showed for a majority of states the Breit interaction changed the values of the q factors only at the level of a few percent. For this reason all results which we discuss below are obtained in the pure Coulomb approximation.

B. Ground multiplet 5D_J

The ground-state FS transitions in midinfrared and far-infrared were observed in emission for different redshifts for a number of atoms and ions (see, e.g., [19–21]). The infrared FS lines of the neutral iron have not been detected yet in astronomical objects. But such a detection is expected in extragalactic objects at a new generation of telescopes such as the Stratospheric Observatory for Infrared Astronomy and Far Infrared and Submillimeter Telescope.

We start the discussion from the results obtained for transitions between the states of the ground multiplet. The CI space corresponds to SD excitations from the configuration $3d^64s^2$. In Table I we present results obtained for the $[6spdf]$ basis set for energy levels, g factors, and q factors for transitions from the ground state 5D_4 .

A method to use these FS transitions to study α variation at very high redshifts was suggested in Ref. [23]. This method crucially depends on the differences of the dimensionless sensitivity coefficients defined as

$$Q_{J,J-1} = (q_J - q_{J-1})/\omega_{J,J-1}, \tag{3}$$

where $\omega_{J,J-1} = E_J - E_{J-1}$ is the frequency of the FS transition $J \leftrightarrow J-1$.

TABLE I. Energy levels (cm⁻¹), g factors, and q factors (cm⁻¹) for the $(3d^64s^2)$ a^5D_J states. The values are obtained for the $[6spdf]$ basis set.

	Expt. ^a		Calculations		
	Energy	g	Energy	g	q
a^5D_4	0	1.5002	0	1.4996	0
a^5D_3	416	1.5003	407	1.4994	413
a^5D_2	704	1.5004	694	1.5001	684
a^5D_1	888	1.5002	879	1.4999	853
a^5D_0	978		969		935

^aNIST, Ref. [22].

It was shown in [23] that for the levels of the $^{2S+1}L_J$ multiplet the difference, ΔQ , between the dimensionless sensitivity coefficients $Q_{J,J-1}$ and $Q_{J-1,J-2}$ is given by the following formula

$$\Delta Q \equiv Q_{J,J-1} - Q_{J-1,J-2} = \frac{J-1}{J} \left(\frac{\omega_{J,J-1}}{\omega_{J-1,J-2}} \right) - 1, \tag{4}$$

which links ΔQ to the experimentally observed FS transition frequencies. This analytical expression is valid up to the terms of the order of $(\alpha Z)^4$. Note, that in the first order in the spin-orbit interaction the left-hand side of Eq. (4) turns to zero. For this reason ΔQ is very sensitive to the ratio of the FS transition frequencies.

As is seen from Table I we reproduce the FS intervals with a few percent accuracy. The uncertainties of the q factors listed in Table I can also be estimated at the level of a few percent. Such inaccuracies in calculation of the FS transition frequencies and q factors, though small, are sufficient to result in significant differences between the values of ΔQ calculated with use of Eq. (3) and obtained from Eq. (4).

To illustrate it we present in Table II the differences of the sensitivity coefficients (ΔQ) of the FS lines within the ground multiplet a^5D_J obtained by both methods mentioned above. The corresponding entries in Table II are denoted as Eqs. (3) and (4). In the first case we used the q factors and the calculated transition frequencies from Table I. In the second case the Eq. (4) and the experimental frequencies were used.

Comparing these results we see that there is only qualitative agreement between numerical and analytical approaches. For instance, Eq. (4) predicts decreasing of ΔQ with decreasing

TABLE II. ΔQ for the FS lines within the ground multiplet a^5D_J . Numerical results are calculated using Eq. (3) for the basis set $[6spdf]$. Analytical expression (4) is applied to the experimental frequencies as in Ref. [23].

(J_a, J'_a)	(J_b, J'_b)	Equation (3)	Equation (4)
(2,3)	(3,4)	0.067	0.083
(1,2)	(2,3)	0.027	0.043
(0,1)	(1,2)	0.018	0.024

TABLE III. Energy levels (cm^{-1}), g factors, and q factors (cm^{-1}) for the odd-parity energy levels of the $3d^64s4p$ configuration. The values are obtained for the $[6spdf]$ basis set.

	Expt. ^a		Calculations			
	Energy	g	Energy	g	q	q^b
$z^7D_5^o$	19351	1.597	20204	1.599	722	490
$z^7D_4^o$	19562	1.642	20415	1.649	895	662
$z^7D_3^o$	19757	1.746	20613	1.749	1096	891
$z^7F_5^o$	22846	1.498	22988	1.500	1004	827
$z^7F_4^o$	22997	1.493	23148	1.501	1155	982
$z^7F_3^o$	23111	1.513	23269	1.501	1269	1103
$z^7P_4^o$	23711	1.747	23903	1.749	744	491
$z^7P_3^o$	24181	1.908	24383	1.915	1211	983
$z^5D_4^{oc}$	25900	1.502	26065	1.497	1032	999
$z^5D_3^o$	26140	1.500	26302	1.496	1239	1223
$z^5F_5^{oc}$	26875	1.399	26820	1.400	927	880
$z^5F_4^o$	27167	1.355	27114	1.353	1224	1180
$z^5F_3^o$	27395	1.250	27338	1.255	1441	1402
$z^5P_3^{oc}$	29056	1.657	28653	1.665	1008	859
$z^3F_4^o$	31307	1.250	31216	1.250	1177	1267
$z^3F_3^o$	31805	1.086	31703	1.093	1665	1808
$z^3D_3^o$	31323	1.321	31177	1.324	1338	1456
$y^5P_3^o$	36767	1.661	38411	1.665	910	
$x^5D_4^{oc}$	39626	1.489	41328	1.499	2163	1680
$x^5D_3^o$	39970	1.504	41753	1.494	2632	
$x^5F_5^{oc}$	40257	1.390	40476	1.399	1725	1042
$x^5F_4^o$	40594	1.328	40839	1.347	2158	
$x^5F_3^o$	40842	1.254	41077	1.254	2416	

^aNIST, Ref. [22].

^bReference [15].

^cStates observed in the quasar absorption spectra.

ing J . When we use Eq. (3) we observe the same behavior. At the same time, quantitatively, a disagreement is rather significant. We think that numerical errors in computing the q factors and the FS transition frequencies are more essential for calculation of ΔQ than the terms $\sim(\alpha Z)^6$ (and higher) neglected in Eq. (4). For this reason we consider the values obtained from Eq. (4) as more correct.

C. Odd parity levels

The transitions from the ground state to the odd-parity states are observed in absorption in the spectra of quasars. The results of the eight-electron CI calculations of the energy levels, g factors, and q factors for the odd-parity states of the $3d^64s4p$ configuration of Fe I are listed in Table III. We have carried out calculations for the three basis sets $[(4-6)spdf]$. The CI space for each basis set corresponds to SD excitations from two configurations $3d^64s4p$ and $3d^74p$. The agreement between theoretical and experimental energy levels was systematically improved with increasing the basis set and best results were obtained for the longest $[6spdf]$ basis set. In Table III we present the results obtained for the largest

$[6spdf]$ basis set. We restrict ourselves by consideration of the states with total angular momenta $J=3, 4$, and 5 because only to these states there are strong electric-dipole transitions from the ground ($3d^64s^2\ ^5D_4$) state.

Comparing the q factors found in this work with the results obtained in Ref. [15] we see reasonable agreement between them for majority of the states. At the same time some differences reach 40%. One of the reasons for these discrepancies is the strong configuration interaction for certain levels that significantly influences the q factors. For instance, for the astrophysically interesting $x^5D_4^o$ and $x^5F_5^o$ states of the $3d^64s4p$ configuration we obtained in one-configurational approximation the following q factors: $q(x^5D_4^o)=835\ \text{cm}^{-1}$ and $q(x^5F_5^o)=861\ \text{cm}^{-1}$. As is seen from Table III these values are more than two times smaller than those obtained for the $[6spdf]$ basis set when a large number of configurations was included into consideration. At the same time we see that even for the largest basis set the number of configurations taken into account is still not sufficient to correctly reproduce the order of certain states. For instance, the energy levels of the $x^5D_4^o$ multiplet lays higher than the energy levels of the $x^5F_3^o$ multiplet. Since this range of spectrum is very dense and there are many nearby levels with the same total angular momenta, it can lead to incorrect interaction of the mentioned states with their neighbors.

Now we will discuss the odd-parity states of the $3d^74p$ configuration. Correct calculation of different properties of these states is more difficult than calculation of the states belonging to the $3d^64s4p$ configuration. First, the states of the $3d^74p$ configuration are located higher in energy than the majority of the states of the $3d^64s4p$ configuration considered by us. Second, the energy levels of the $3d^74p$ configuration belonging to different multiplets are located very close to each other and strongly interact to each other. An additional problem is that the DHF equations were solved self-consistently for the configuration $3d^64s^2$. The configuration $3d^74p$ differs more significantly from it than the configuration $3d^64s4p$, in particular, by the presence of an extra d electron on the $3d$ shell. As a consequence, it is more difficult to reproduce the correct transition frequencies from the states of the $3d^74p$ configuration to the ground state. As our analysis shows these calculated frequencies tend to be larger than the experimental ones.

To investigate how different properties of these states will change when the basis set is increased from $[4spdf]$ to $[6spdf]$, we have carried out the calculations for all these basis sets. The agreement between theoretical and experimental frequencies was at the level of 5%–10%. As it turned out the best agreement was achieved for the $[5spdf]$ basis set. This obviously indicates that for this configuration we are still far from saturating the CI space. In Table IV we present energy levels, g , and q factors obtained for this basis set.

As is seen from Table IV the agreement between theoretical and experimental energy levels is worse than it was for the states of the $3d^64s4p$ configuration but nevertheless the largest difference does not exceed 7%. An interesting fact is that the agreement between q factors obtained by us and by Dzuba and Flambaum [15] is (on average) better than for the states of the $3d^64s4p$ configuration.

TABLE IV. Energy levels (cm⁻¹), g factors, and q factors (cm⁻¹) for the states of the $3d^74p$ configuration. The values are obtained for the $5spdf$ basis set. Results obtained in Ref. [15] are given for comparison.

	Expt. ^a		Calculations			
	Energy	g	Energy	g	q	q^b
$y^5D_4^o$	33096	1.496	34766	1.499	1794	2494
$y^5D_3^o$	33507	1.492	35140	1.500	2118	3019
$y^5F_5^o$	33695	1.417	35750	1.399	2306	2672
$y^5F_4^o$	34040	1.344	36069	1.348	2585	3021
$y^5F_3^o$	34329	1.244	36338	1.248	2836	3317
$z^5G_5^o$	34782	1.218	37164	1.212	2736	3024
$z^5G_4^o$	35257	1.103	37646	1.088	3196	3520
$z^5G_3^o$	35612	0.887	38038	0.855	3563	3864
$z^3G_5^o$	35379	1.248	37806	1.256	3343	3340
$z^3G_4^o$	35768	1.100	38142	1.120	3640	3697
$z^3G_3^o$	36079	0.791	38401	0.821	3909	4096
$y^3F_4^o$	36686	1.246	38703	1.245	3083	3085
$y^3F_3^o$	37162	1.086	39155	1.091	3447	3487
$y^3D_3^o$	38175	1.324	39904	1.321	3079	

^aNIST, Ref. [22].

^bReference [15].

Analyzing the q factors presented in Tables III and IV we see that the former are (on average) smaller than the latter. It has simple explanation because the transition between $3d^64s^2$ and $3d^64s4p$ configurations is basically a one-electron $4s$ - $4p$ transition. The transition between $3d^64s^2$ and $3d^74p$ configurations is due to simultaneous $4s$ - $4p$ and $4s$ - $3d$ one-electron transitions. As was shown in [24], when α is changing toward its nonrelativistic limit $\alpha=0$, changes of one-electron energies of s and d states are differently directed. It leads to increasing the q factors.

Note that the states nominally belonging to the $3d^74p$ configuration are formed, as a rule, as a result of strong mixing of $3d^64s4p$ and $3d^74p$ configurations. An admixture of the $3d^64s4p$ configuration to the $3d^74p$ configuration leads to opening a strong electric-dipole transitions from the states of the $3d^74p$ configuration to the ground state. It allows one to make these transitions observable.

Using the results obtained for the $[4spdf]$, $[5spdf]$, and $[6spdf]$ basis sets we are able to estimate uncertainties of the calculated q factors. We roughly estimate the uncertainty as the difference between largest and smallest values of the q factors found for the three basis sets mentioned above. Such conservative estimate allows us to say that the q factors for the odd-parity energy levels listed in Tables III and IV are within 20% accuracy.

III. ISOTOPE SHIFT CALCULATION IN Fe II AND Fe I

A. Method

It is known that the energy levels of two isotopes of any element are shifted relative to each other. Total IS is usually divided into mass shift (MS) and field shift. The former is

due to nuclear recoil and the latter is caused by the finite size of the nuclear charge distribution. For light elements the field shift is much smaller than the mass shift and usually can be neglected.

Let us compare the mass and field shifts for two most abundant isotopes of iron ^{56}Fe and ^{54}Fe . The field shift constant F was recently calculated for the $4s \rightarrow 4p$ transition for Ti II to be about $|F| \approx 0.4 \text{ GHz/fm}^2$ [25]. Since Ti II, as well as Fe, is an element with open $3d$ shell its properties are similar to those of Fe. Respectively, we can expect similar value of the constant F for $4s \rightarrow 4p$ transitions in Fe I and Fe II.

The field shift is given by

$$|\delta\omega|_{\text{FS}} = |F\delta\langle r_{\text{nuc}}^2 \rangle| \sim 0.4 \text{ GHz} \times 0.3 \text{ fm}^2 \sim 0.1 \text{ GHz}, \quad (5)$$

where we used nuclear radii from [26]. According to our calculations the MS constants $|k_{\text{MS}}| \approx 1000 \text{ GHz}$ and

$$|\delta\omega|_{\text{MS}} = \left| k_{\text{MS}} \left(\frac{1}{54} - \frac{1}{56} \right) \right| \approx 0.6 \text{ GHz}. \quad (6)$$

Thus, the field shift is expected to be an order of magnitude smaller than the MS and we disregard it in the following.

In relativistic approximation the mass-shift operator can be represented in the form of expansion in αZ . In Ref. [27] the following expression was obtained for this operator involving first two terms of the expansion over αZ ,

$$H_{\text{MS}} = \frac{1}{2M} \sum_{i,k} \left(\mathbf{p}_i \mathbf{p}_k - \frac{\alpha Z}{r_i} [\boldsymbol{\alpha}_i + (\boldsymbol{\alpha}_i \mathbf{n}_i) \mathbf{n}_i] \mathbf{p}_k \right), \quad (7)$$

where M is the nuclear mass, \mathbf{p}_i is the momentum operator, $\mathbf{n}_i = \mathbf{r}_i / r_i$, and $\boldsymbol{\alpha}_i$ is the Dirac matrices of the i th electron.

Equation (7) can be symmetrized over variables of i th and k th electrons and written in the following form [13]:

$$H_{\text{MS}} = \frac{1}{2M} \sum_{i,k} \left(\mathbf{p} - \frac{\alpha Z}{2r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \mathbf{n}) \mathbf{n}] \right)_i \times \left(\mathbf{p} - \frac{\alpha Z}{2r} [\boldsymbol{\alpha} + (\boldsymbol{\alpha} \cdot \mathbf{n}) \mathbf{n}] \right)_k. \quad (8)$$

This equation differs from Eq. (7) only by the terms $\sim (\alpha Z)^2$. Equation (8) is more convenient for CI calculations because it is symmetric in electrons. This allows us to add it to the Coulomb integrals.

Using Eq. (8) we are able to calculate the isotope shift in the frequency, $\delta\omega^{A,A'}$, of a transition between two isotopes with mass numbers A and A' . Neglecting the field shift the expression for $\delta\omega^{A,A'}$ can be written as

$$\delta\omega^{A,A'} = \omega^A - \omega^{A'} \approx (k_{\text{NMS}} + k_{\text{SMS}}) \left\{ \frac{1}{A} - \frac{1}{A'} \right\}. \quad (9)$$

The first term in curly brackets characterizes so-called normal mass shift (NMS), while the second is the specific mass shift (SMS). In terms of Eq. (8) the NMS term is determined by the expression with $i=k$ and the SMS term is determined by the expression with $i \neq k$.

TABLE V. Fe II: Comparison of the relativistic and nonrelativistic forms of the MS operator.

Configuration	Level	Nonrelativistic		Relativistic	
		k_{SMS}	k_{NMS}	k_{SMS}	k_{NMS}
$3d^64s$	${}^6D_{9/2}$	0.0	0.0	0.0	0.0
	${}^6D_{7/2}$	-18.2	6.2	6.6	-2.5
	${}^6D_{5/2}$	-31.6	10.7	10.9	-4.1
	${}^6D_{3/2}$	-40.8	13.9	13.6	-5.0
	${}^6D_{1/2}$	-46.2	15.8	15.1	-5.6
$3d^64p$	${}^6D_{9/2}^o$		614.6	572.0	609.3
	${}^6D_{7/2}^o$		617.9	576.3	607.0
	${}^6F_{11/2}^o$		675.8	752.6	671.1
	${}^6F_{9/2}^o$		678.3	759.0	667.1
	${}^6F_{7/2}^o$		680.3	761.5	664.2
	${}^6P_{7/2}^o$		686.7	467.5	680.0

It is worth noting that the use of relativistic MS operator is very important for calculating IS for the transitions between the FS energy levels of the ground multiplet. Table V illustrates the role of these corrections to the MS operator. As is seen from the table the size of these corrections is about the same for the fine-structure transitions and for optical transitions, while nonrelativistic values are very different. Thus, including the relativistic corrections is crucial for the case of the FS energy levels and is unimportant for the optical transitions. This problem is discussed in more detail in [13].

For transitions from the states of other multiplets to the ground state the IS is less sensitive to the relativistic corrections. For such transitions the coefficient k_{NMS} can be found with a good accuracy from its nonrelativistic expression $k_{\text{NMS}} = -\omega/1823$. The value 1823 is the ratio of the atomic mass unit to the electron mass.

Technically the isotope shift of an energy level can be found as follows. The operator H_{MS} can be added to the many-body Hamiltonian H with an arbitrary coefficient λ ,

$$H_\lambda = H + \lambda H_{\text{MS}}. \quad (10)$$

When the eigenvalue E_λ of the Hamiltonian H_λ is found, the IS correction to the energy can be obtained as

$$\Delta E = \left. \frac{dE_\lambda}{d\lambda} \right|_{\lambda=0} \approx \frac{E_{+\lambda} - E_{-\lambda}}{2\lambda}. \quad (11)$$

The parameter λ should be chosen from the conditions of numerical stability and smallness of the nonlinear terms. In our calculations $\lambda/(2M)$ was put to be 0.001.

B. Results for Fe I

Analysis of the energies and q factors for Fe I obtained with the basis sets $[4spdf]$, $[5spdf]$, and $[6spdf]$ shows that the differences in the results appeared to be not very large. At the same time a computational cost increases drastically with increasing basis set. For this reason we have carried out cal-

TABLE VI. Fe I: Experimental and theoretical transition frequencies ω of the even- and odd-parity states respective to the ground state (in cm^{-1}), k_{SMS} (in GHz) and k_{NMS} (in GHz) are presented. The values are obtained for the $[4spdf]$ basis set.

Configuration	Level	$\omega_{\text{expt.}}^a$	$\omega_{\text{theor.}}$	k_{SMS}	k_{NMS}
$3d^64s^2$	a^5D_4	0	0	0	0
	a^5D_3	416	409	6	-3
	a^5D_2	704	697	10	-5
	a^5D_1	888	883	12	-6
	$3d^64s4p$	$z^7D_5^o$	19351	20550	557
$z^7D_4^o$		19562	20759	562	322
$z^7D_3^o$		19757	20972	565	325
$z^7F_5^o$		22846	22190	610	376
$z^7F_4^o$		22997	22364	614	378
$z^7F_3^o$		23111	22498	616	380
$z^7P_4^o$		23711	22727	650	390
$z^7P_3^o$		24181	23199	658	398
$z^5D_4^o$		25900	25374	766	426
$z^5D_3^o$		26140	25617	769	430
$z^5F_5^o$		26875	25885	734	442
$z^5F_4^o$		27167	26189	743	447
$z^5F_3^o$		27395	26416	748	450
$z^5P_3^o$		29056	27059	792	478
$z^3F_4^o$		31307	30147	981	515
$z^3F_3^o$	31805	30624	988	523	
$z^3D_3^o$	31323	29910	1016	515	
$y^5P_3^o$	36767	38430	471	605	
$x^5D_4^o$	39626	40609	2326	652	
$x^5D_3^o$	39970	41034		657	
$x^5F_5^o$	40257	39620	1749	662	
$x^5F_4^o$	40594	39982	1810	668	
$x^5F_3^o$	40842	40258		672	
$3d^74p$	$y^5D_4^o$	33096	35157	1568	544
	$y^5D_3^o$	33507	35520	1529	551
	$y^5F_5^o$	33695	36251	2287	554
	$y^5F_4^o$	34040	36571	2279	560
	$y^5F_3^o$	34329	36837	2257	565
	$z^5G_5^o$	34782	38100	3508	572
	$z^5G_4^o$	35257	38499	3499	580
	$z^5G_3^o$	35612	38822	3506	586
	$z^3G_5^o$	35379	38578	3514	582
	$z^3G_4^o$	35768	38913	3549	588
	$z^3G_3^o$	36079	39271	3531	593
	$y^3F_4^o$	36686	39116	3521	603
	$y^3F_3^o$	37162	39507	3535	611
	$y^3D_3^o$	38175	39933	3456	628

^aNIST, Ref. [22].

culations of the isotope shifts for the transitions from the even-parity states of the ground multiplet to the ground state and from the odd-parity states of the $3d^64s4p$ and $3d^74p$ configurations to the ground state using the $[4spdf]$ basis set.

TABLE VII. Fe II: Experimental and theoretical transition frequencies ω of the even- and odd-parity states respective to the ground state (in cm^{-1}), k_{SMS} (in GHz), and k_{NMS} (in GHz) are presented. $k_{\text{MS}}=k_{\text{SMS}}+k_{\text{NMS}}$. The values are obtained for the $[7spdf]$ basis set.

Configuration	Level	$\omega_{\text{expt.}}^{\text{a}}$	$\omega_{\text{theor.}}$	k_{SMS}	k_{NMS}	k_{MS}	Ref. [12]
$3d^64s$	${}^6D_{9/2}$	0	0	0	0	0	
	${}^6D_{7/2}$	385	375	7	-3	4	
	${}^6D_{5/2}$	668	653	11	-4	7	
	${}^6D_{3/2}$	863	846	14	-5	9	
	${}^6D_{1/2}$	977	960	15	-6	9	
$3d^64p$	${}^6D_{9/2}^o$	38459	37373	572	632	1204	1800(600)
	${}^6D_{7/2}^o$	38660	37573	576	636	1212	1800(600)
	${}^6F_{11/2}^o$	41968	41097	753	690	1443	1900(600)
	${}^6F_{9/2}^o$	42115	41247	759	693	1452	1900(600)
	${}^6F_{7/2}^o$	42237	41370	762	695	1457	
	${}^6P_{7/2}^o$	42658	41760	468	702	1170	1800(600)
	${}^6D_{7/2}^o$	38660	37573	576	636	1212	
	${}^6F_{7/2}^o$	42237	41370	762	695	1457	
	${}^6P_{7/2}^o$	42658	41760	468	702	1170	
	${}^4F_{7/2}^o$	44754	44044	737	736	1473	2010(1200)
	${}^4D_{7/2}^o$	44447	44270	728	731	1459	
	${}^4G_{7/2}^o$	60957	62766	626	1002	1628	
	${}^4H_{7/2}^o$	61157	62894	947	1006	1953	
	${}^4F_{7/2}^o$	62066	64017	305	1021	1326	
	${}^2G_{7/2}^o$	62322	64217	526	1025	1551	
$3d^54s4p$	${}^8P_{7/2}^o$	52583	49115	-3164	865	-2299	
	${}^6P_{7/2}^o$	62172	59245	-3074	1022	-2052	-2010(1200)

^aNIST, Ref. [22].

In the first case for calculation of both k_{SMS} and k_{NMS} we used the relativistic MS operator given by Eq. (8). In the second case the specific mass shift k_{SMS} was calculated in the relativistic approximation, while the normal mass shift was obtained from the simple formula $k_{\text{NMS}}=-\omega/1823$ with use of the experimental frequencies.

Table VI presents the results obtained for k_{SMS} and k_{NMS} . Analyzing these results we see that the total mass shift $k_{\text{MS}}=k_{\text{SMS}}+k_{\text{NMS}}$ is small for the transitions from the fine-structure components of the ground multiplet to the ground state.

As it was shown in Ref. [25] the isotope shifts in Ti II for certain levels are strongly influenced by core-valence correlations disregarded in our approach. They contribute to k_{SMS} at the level of 50% or even more. The main configuration of Ti II is $3d^24s$. Of course, the core of Ti II is less rigid than that of Fe I and the role of core-valence correlations should be greater. Nevertheless, we expect that a treatment of the core-valence correlations will lead to more significant changes of k_{SMS} than inclusion of the relativistic corrections due to the Breit interaction between electrons.

C. Results for Fe II

The method of calculation of different properties of Fe II is similar to that for the neutral iron. The results of calculation of the q factors for a number of the odd-parity states

were reported in Refs. [18,28]. All details of the method of calculations can be found in [18]. Here we only briefly recapitulate its main features.

At first we solved the Dirac-Fock equations to find core orbitals $1s, \dots, 3p_{3/2}$ and valence orbitals $3d_{3/2}, 3d_{5/2}, 4p_{1/2}, 4p_{3/2}$. Then we added virtual orbitals, which were constructed using the procedure described in Sec. II. The basis set used for seven-electron CI calculations included $s, p, d,$ and f orbitals with principle quantum number $n \leq 7$ designated as $[7spdf]$. Configuration space was formed by SD excitations from the configurations $3d^64s, 3d^64p,$ and $3d^54s4p$.

The method of calculations of the IS remains the same as for Fe I. The results of the seven-electron CI calculation of the IS in Fe II are listed in Table VII. To the best of our knowledge the only calculation of the IS for certain transitions in Fe II was carried out in [12]. We see reasonable agreement between the results obtained in this work with the values found in Ref. [12].

IV. CONCLUSION

We have calculated relativistic frequency shifts (q factors) for a number of transitions from the even- and odd-parity states of Fe I to the ground state. The calculations were carried out for the three basis sets $[4spdf], [5spdf],$ and

[6*spdf*]. Comparing the results obtained for these basis sets we could estimate the accuracy of the q factors for the odd-parity energy levels listed in Tables III and IV at the level of 20%. The accuracy of the q factors for the transitions from the even-parity states of the ground multiplet to the ground state is significantly higher. We estimate it at the level of a few percent.

The certain odd-parity states are astrophysically interesting because they were observed in quasar absorption spectra. Due to strong configuration interaction the magnitudes of the q factors vary significantly between the states. This makes Fe I a very attractive candidate to search for hypothetical α variation.

We also computed the mass isotope shifts for Fe I and Fe II for the [4*spdf*] basis set. Comparing the results obtained for Fe II with the values of [12] we see a reasonable agreement between them.

ACKNOWLEDGMENTS

We would like to thank V. Dzuba, S. Levshakov, and P. Molaro who brought our attention to this problem. This work was supported in part by the Russian Foundation for Basic Research under Grants No. 07-02-00210-a and No. 08-02-00460-a, and by DFG under Grants No. SFB 676 Teilprojekt C4 and No. RE 353/48-1.

-
- [1] E. García-Berro, J. Isern, and Y. A. Kubyshev, *Astron. Astrophys. Rev.* **14**, 113 (2007).
- [2] E. J. Copeland, M. Sami, and S. Tsujikawa, *Int. J. Mod. Phys. D* **15**, 1753 (2006).
- [3] M. T. Murphy, J. K. Webb, and V. V. Flambaum, *Mon. Not. R. Astron. Soc.* **345**, 609 (2003).
- [4] R. Quast, D. Reimers, and S. A. Levshakov, *Astron. Astrophys.* **415**, L7 (2004).
- [5] R. Srikanth, H. Chand, P. Petitjean, and B. Aracil, *Phys. Rev. Lett.* **92**, 121302 (2004).
- [6] S. A. Levshakov, P. Molaro, S. Lopez, S. D'Odorico, M. Centurion, P. Bonifacio, I. I. Agafonova, and D. Reimers, *Astron. Astrophys.* **466**, 1077 (2007).
- [7] V. D'Odorico, *Astron. Astrophys.* **470**, 523 (2007).
- [8] R. Quast, D. Reimers, and R. Baade, *Astron. Astrophys.* **477**, 443 (2008).
- [9] P. Molaro and S. A. Levshakov (private communications).
- [10] S. A. Levshakov, *Mon. Not. R. Astron. Soc.* **269**, 339 (1994).
- [11] D. A. Varshalovich, A. Y. Potekhin, and A. V. Ivanchik, *Phys. Scr.* **T95**, 76 (2001).
- [12] M. G. Kozlov, V. A. Korol, J. C. Berengut, V. A. Dzuba, and V. V. Flambaum, *Phys. Rev. A* **70**, 062108 (2004).
- [13] V. A. Korol and M. G. Kozlov, *Phys. Rev. A* **76**, 022103 (2007).
- [14] M. Ascoli, E. E. Eyler, D. Kawall, and D. DeMille, *Meas. Sci. Technol.* **19**, 045602 (2008); M. Ascoli, E. E. Eyler, D. Kawall, and D. DeMille, e-print arXiv:0709.4032.
- [15] V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **77**, 012514 (2008).
- [16] P. Bogdanovich, *Lith. Phys. J.* **31**, 79 (1991).
- [17] M. G. Kozlov, S. G. Porsev, and V. V. Flambaum, *J. Phys. B* **29**, 689 (1996).
- [18] S. G. Porsev, K. V. Koshelev, I. I. Tupitsyn, M. G. Kozlov, D. Reimers, and S. A. Levshakov, *Phys. Rev. A* **76**, 052507 (2007).
- [19] L. T. Greenberg, P. Dyal, and T. R. Geballe, *Astrophys. J.* **213**, L71 (1977).
- [20] A. F. M. Moorwood, P. Salinari, I. Furniss, R. E. Jennings, and K. J. King, *Astron. Astrophys.* **90**, 304 (1980).
- [21] A. Weiß, C. Henkel, D. Downes, and F. Walter, *Astron. Astrophys.* **409**, L41 (2003).
- [22] NIST, Atomic Spectra Database (http://physics.nist.gov/cgi-bin/AtData/main_asd).
- [23] M. G. Kozlov, S. G. Porsev, S. A. Levshakov, D. Reimers, and P. Molaro, *Phys. Rev. A* **77**, 032119 (2008).
- [24] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, *Phys. Rev. A* **59**, 230 (1999).
- [25] J. C. Berengut, V. V. Flambaum, and M. G. Kozlov, *J. Phys. B* **41**, 235702 (2008).
- [26] I. Angeli, *At. Data Nucl. Data Tables* **87**, 185 (2004).
- [27] V. M. Shabaev and A. N. Artemyev, *J. Phys. B* **27**, 1307 (1994).
- [28] V. A. Dzuba, V. V. Flambaum, M. G. Kozlov, and M. Marchenko, *Phys. Rev. A* **66**, 022501 (2002).