Transition frequency shifts with fine-structure-constant variation for Fe II: Breit and core-valence correlation corrections

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Transition frequencies of Fe II ion are known to be very sensitive to variation of the fine-structure constant α. The resonance absorption lines of Fe II from objects at cosmological distances are used in a search for the possible variation of α in the course of cosmic time. In this paper we calculated the dependence of the transition frequencies on α^2 (q factors) for Fe II ion. We found corrections to these coefficients from valence-valence and core-valence correlations and from the Breit interaction. Both the core-valence correlation and Breit corrections to the q factors appeared to be larger than had been anticipated previously. Nevertheless our calculation confirms that the Fe II absorption lines seen in quasar spectra have large q factors of both signs and thus the ion Fe II alone can be used in the search for the α variation at different cosmological epochs.

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I. INTRODUCTION

Recently discovered acceleration of the universe (for a review, see [1]) is usually regarded as evidence for the existence of dark energy. Cosmological evolution of the dark energy may cause variations of fundamental constants, such as the fine-structure constant α and proton to electron mass ratio $\mu=m_p/m_e$ (see, e.g., [2], and references therein). Different models predict different behavior of the coupling constants and it is extremely important to measure α at different cosmological epochs.[1]

Because of the relativistic effects in atoms their transition frequencies depend on αZ, where Z is an atomic number. Therefore, one can study space-time variation of α by comparing atomic frequencies for distant objects in the universe with their laboratory values. To do this one needs to calculate so-called q factors for the atomic transitions, which are defined as follows:

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

Generally, q factors may have different signs and scale with an atomic number as Z^2 (see [3]). That allows one to look for α variation by comparing transition frequencies of heavy and light ions [4,5]. However, under astrophysical conditions the relative fractions of different ions depend on the gas density fluctuations within the absorbing cloud and thus the measured positions of the absorption lines are affected by irregular Doppler velocity shifts of the bulk motions leading to an additional noise in the $\Delta\alpha/\alpha$ measurements [6,7].

Therefore, one can try to find an atom, where q factors for different transitions have different signs and large absolute values. In Ref. [9] it was shown that the line 1608 Å in Fe II has a large negative q factor, while other UV resonance lines have large positive q factors. An additional advantage of Fe II is the relatively small values of isotope shifts [8]. This fact was used in [6,10–12] to suggest the single ion differential α measurement (SIDAM) procedure, which is less sensitive to uncertainties inherent to the method applied in [4,5] and allows us to measure $\Delta\alpha/\alpha$ at a single redshift z with a sufficiently high accuracy ($\sigma_{\Delta\alpha/\alpha} \sim 10^{-6}$–$10^{-5}$).

Here we report new calculations of the q factors for Fe II with a more accurate account for relativistic effects and electronic correlations. In particular, we studied corrections to the q factors from the Breit interaction and the core-valence correlations. We found that both corrections are noticeable but do not change the previous conclusion [9] that Fe II has large q factors of both signs.

II. METHOD OF CALCULATION

In order to calculate q factors one can solve an atomic relativistic eigenvalue problem for different values of α. For example, if we calculate atomic frequency $\omega_\pm$ for two values $x=\pm 1/8$ of the parameter x in Eq. (1), the corresponding q factor is given by

$$q = 4(\omega_+ - \omega_-). \tag{2}$$

The choice of $x=\pm 1/8$ is usually sufficiently small to neglect nonlinear corrections and sufficiently large to make calculations numerically stable. The exceptions may occur for the strongly interacting levels. Such cases require special consideration.

The Fe II ion has ground state configuration $[{\rm Ar}]3d^6 4s$ with seven electrons in open shells, hence it has a rather dense and complicated spectrum, particularly in the astrophysically important region above 60 000 cm^{-1} from the ground state. Calculations for Fe II are very difficult because of the large number of valence electrons and high density of the spectrum [3,9,14,15].

[1]Each cosmological epoch is characterized by the redshift parameter z, which is defined in the spectral observations as $z=(\lambda_{\rm obs}-\lambda_{\rm lab})/\lambda_{\rm lab}$, with $\lambda_{\rm obs}, \lambda_{\rm lab}$ being correspondingly the observational and laboratory wavelengths of an atomic transition. Currently we observe objects with z ranging from 0 (local universe) up to 7.

We use Dirac-Coulomb and Dirac-Coulomb-Breit "no pair" Hamiltonians. At the first stage we use the frozen-core approximation and solve valence eigenvalue problem by means of the configuration interaction (CI) method. Using Eq. (2) it is important that the CI space is the same for two values of x. When four-component finite basis sets are used to solve many-electron Dirac equations, the basic orbitals depend on α. The incompleteness of the CI space can introduce some error for q factors. To check if this error is small we make several CI calculations with different basis sets.

At first we solve Dirac-Fock equations with the code [16] to find core orbitals $1s,\ldots,3p_{3/2}$ and valence orbitals $3d_{3/2},3d_{5/2},4s,4p_{1/2},4p_{3/2}$. Then we add virtual orbitals, which are constructed using the method described in [17,18]. In this method an upper component of virtual orbitals is formed from the previous orbital of the same symmetry by multiplication by some monotone function of radial variable r. The lower component is then formed using a kinetic balance condition. (An alternative method to form basis sets was suggested in [19]). Our basis sets include s, p, d, and f orbitals with principle quantum number $n \leqslant N$ and are designated as $[Nspdf]$. Configuration space is formed by single and double (SD) excitations from the configurations $3d^64s$, $3d^64p$, and $3d^54s4p$. Respective dimensions of the CI space are significantly larger than in previous calculations [3,9].

In order to study the Breit correction to the q factors we do calculations for Coulomb, Coulomb-Gaunt, and Coulomb-Breit approximations, where Gaunt approximation accounts for the magnetic interaction and Breit interaction also includes a retardation term. We have found that due to the large number of valence electrons and relative smallness of the nuclear charge Z it is necessary to include Breit correction to the valence-valence interactions as well as to the core-valence and core-core ones.

In our calculation the Ar-like core is rather small and rigid, with binding energies $|\varepsilon|>3$ a.u. For this reason one can expect that corrections from core excitations should be small. The same conclusion follows from the relatively good agreement between theoretical spectra in the frozen core approximation and the experiment [33]. On the other hand, correlations between core electrons and valence $3d$ electrons are enhanced. For this reason the core-valence correlations require thorough investigation.

Usually one can use the many-body perturbation theory (MBPT) to account for core-valence correlations. Unfortunately, it is difficult to implement MBPT for atoms with open d shells because valence d shell electrons belong to the previous atomic shell. That leads to a much stronger interaction between valence d electrons and uppermost core electrons [20–22]. Because of that it is impractical to use the $V^{N_{\rm core}}$ approximation, where MBPT is much simpler than in the case of V^N potential with $N \neq N_{\rm core}$. Generally MBPT includes a large class of the so-called subtraction diagrams, which cancel out for $V^{N_{\rm core}}$ approximation. That not only increases the complexity of calculations but also makes them less stable because of the large cancellations between "normal" and subtraction diagrams [23]. Due to these problems the CI+MBPT method [24], which proved to be rather effective for treating atoms with several s and p electrons in the open shells [25–29], is much less effective here. Because of that we combine the CI+MBPT method with conventional CI calculation for 15 electrons including eight outermost core electrons.

III. RESULTS

A. Valence CI

The results of the seven-electron CI calculation of the spectrum of Fe II are listed in Table I. The CI space for each basis set corresponds to SD excitations from configurations $3d^64s$, $3d^64p$, and $3d^54s4p$. It is convenient to divide all levels presented in Table I into three groups. The first group includes five levels of the even-parity ^6D_J manifold. To the second group we relate the low-lying odd-parity states of the configuration $3d^64p$, namely, $^6D^o_{9/2,7/2}$, $^6F^o_{11/2,9/2}$, and $^6P^o_{7/2}$. Finally, in the third group we include two levels of the configuration $3d^54s4p$ ($^8P^o_{7/2}$ and $^6P^o_{7/2}$) and the closely located states of the configuration $3d^64p$: $^4G^o_{7/2}$, $^4H^o_{7/2}$, and $^4F^o_{7/2}$.

Properties of the even-parity levels from the first group (fine-structure splitting, g and q factors) are rather insensitive to configuration interaction. All these quantities change very weakly with increasing the basis set and the size of the configuration space. An explanation is that the weight of the leading configuration $3d^64s$ for these states is about 95–97 %. A small admixture of other configurations does not influence their properties.

Behavior of the odd levels from the second group is rather similar. It is seen from Table I that g factors of these levels remain practically the same while transition frequencies and q factors change by less than 4% when the basis set is increased from $[5spdf]$ to $[7spdf]$. The weight of the leading configuration $3d^64p$ for the $^6P^o_{7/2}$ state is about 90% and greater than 95% for other states. The levels of different multiplets with the same total angular momentum J are well separated and interact with each other rather weakly.

Comparing calculated transition frequencies for this group of levels with experimental data we see very good agreement. Largest discrepancy does not exceed 3%. There is also a reasonable agreement between the q factors obtained in this work and in Ref. [9]. Except for the state $3d^64p\ ^6P^o_{7/2}$ the differences between q factors are at the level of 1–2 %. For the state $3d^64p\ ^6P^o_{7/2}$ the difference is at the level of 10%. The explanation for this difference is probably the following. Calculation in the paper [9] was done on the basis set $[6spdf]$ and the CI space included SD excitations from the configuration $3d^64p$. In order to accelerate calculations this space was then truncated by excluding nonrelativistic configurations, whose weight in the levels of interest was smaller than 0.5%. Here we do not truncate configuration space and also include the SD excitations from the configuration $3d^54s4p$, which corresponds to triple excitations from the configuration $3d^64p$. Admixture of the configuration $3d^54s4p$ to the state $3d^64p\ ^6P^o_{7/2}$ is at the level of 5%. For this reason the SD excitations from the configuration $3d^54s4p$ appear to be more important for this level.

Table I shows that transition frequencies for the third group of levels also rather weakly depend on the size of the CI space. Comparing the results obtained for the basis sets

TABLE I. Seven-electron CI calculations of transition frequencies ω (in cm^{-1}), g factors, and q factors (in cm^{-1}) for different basis sets. A Dirac-Coulomb Hamiltonian in the frozen-core approximation is used. Transition frequencies and q factors are calculated in respect to the ground state.

		Experiment [33]		[5*spdf*]			[6*spdf*]			[7*spdf*]			Theory [9][a]		
Configuration	Level	ω	g	ω	g	q	ω	g	q	ω	g	q	ω	g	q
$3d^6 4s$	$^6D_{9/2}$	0	1.58	0	1.555	0	0	1.556	0	0	1.555	0	0		0
$3d^6 4s$	$^6D_{7/2}$	385	1.58	382	1.587	384	376	1.586	378	375	1.587	377			
$3d^6 4s$	$^6D_{5/2}$	668	1.665	666	1.657	658	656	1.657	647	653	1.656	644			
$3d^6 4s$	$^6D_{3/2}$	863	1.862	864	1.866	843	849	1.866	829	846	1.866	825			
$3d^6 4s$	$^6D_{1/2}$	977	3.31	980	3.332	950	963	3.333	934	960	3.332	930			
$3d^6 4p$	$^6D^o_{9/2}$	38459	1.542	37218	1.554	1334	37366	1.554	1340	37370	1.554	1334	38352		1361
$3d^6 4p$	$^6D^o_{7/2}$	38660	1.584	37424	1.586	1491	37567	1.586	1492	37570	1.586	1488	38554	1.586	1516
$3d^6 4p$	$^6F^o_{11/2}$	41968		40933	1.454	1478	41094	1.454	1485	41095	1.454	1479	41864		1502
$3d^6 4p$	$^6F^o_{9/2}$	42115	1.43	41088	1.433	1608	41245	1.433	1612	41245	1.433	1607	42012		1623
$3d^6 4p$	$^6P^o_{7/2}$	42658	1.702	41562	1.708	1140	41746	1.709	1136	41758	1.709	1134	42715	1.709	1251
$3d^5 4s4p$	$^8P^o_{7/2}$	52583		48817	1.936	−2058	48919	1.936	−2090	49113	1.936	−2103	54914	1.936	−2085
$3d^6 4p$	$^4G^o_{7/2}$	60957	0.969	62604	0.970	1521	62789	0.962	1468	62773	0.973	1485	63624	0.978	1640
$3d^6 4p$	$^4H^o_{7/2}$	61157	0.720	62578	0.715	1232	62861	0.726	1228	62900	0.718	1171	63498	0.703	1272
$3d^6 4p$	$^4F^o_{7/2}$	62066	1.198	64299	1.227	1166	64307	1.213	1270	64023	1.208	1240	65528	1.252	1062
$3d^5 4s4p$	$^6P^o_{7/2}$	62172	1.68	59011	1.714	−1457	59045	1.714	−1491	59242	1.714	−1506	65750	1.713	−1519

[a]These q factors do not include semiempirical corrections from fitting g factors. The respective corrections are discussed in Sec. III D.

[5*spdf*] and [7*spdf*] we see that a most significant change of ω ($\sim$320 cm^{-1}) is for the $^4H^o_{7/2}$ state. Even here it constitutes only 0.5% of the transition frequency. On the other hand, because of the high density of levels in this part of the spectrum, such changes are comparable to the spacings between different levels with the same J. The Lande factors g for several levels with $J=7/2$ of the configuration $3d^6 4p$ are changing rather strongly from one calculation to another. That signals that these levels interact with each other. However, this interaction does not affect the q factors too much since all these levels have similar dependence on α. The Lande factors of the levels of the configuration $3d^5 4s4p$, in contrast, are very stable. For the most interesting level $^6P^o_{7/2}$ theoretical g factor is somewhat larger than in the experiment. This will be discussed in detail in Sec. III D.

We can sum up, that on the stage of the valence CI calculation there is agreement on the level of few percent between theoretical and experimental frequencies. However, the theory does not reproduce the intervals between levels in the higher part of the spectrum, where the density of states is very high. We see that theoretical frequencies do not change much with the size of the valence space. We can therefore conclude that we are rather close to saturation of the valence CI space and the remaining difference between theory and experiment is mostly caused by neglect of the core-valence correlations. We will discuss this part of the problem in Sec. III C.

B. Breit corrections

The results presented in Table I correspond to the Dirac-Coulomb approximation. As long as we are mostly interested in q factors, which depend on the relativistic corrections to the electronic Hamiltonian, the role of the Breit interaction is enhanced. In order to estimate corresponding corrections we made Dirac-Coulomb and Dirac-Coulomb-Breit calculations of the q factors in the one-configurational approximation. The results of these calculations are given in Table II.

One can see that the Breit corrections to the q factors are non-negligible, particularly for the levels of the configuration $3d^5 4s4p$. It is worth mentioning that, as usual, the magnetic part of the Breit interaction (Gaunt interaction) is significantly larger than the retardation part. On the other hand, the Breit corrections to the valence-valence interactions are comparable to the corrections to core-valence interactions. The reason for that is the relatively small size of the core and the large number of valence $3d$ electrons. Because of that it is important to include the Breit interaction not only in the mean-field potential, but also in the residual two-electron interaction. On the other hand, the Breit corrections to the q factors are sufficiently small (i.e., less than 10%), so that they can be calculated within one-configurational approximation as in Table II. Below we will add this correction to our final result in Table IV.

In Table II we also checked the size of the nonlinear corrections from using Eq. (2) for evaluation of the q factors. For the Dirac-Coulomb approximation we calculated q factors using $x=\pm 1/8$ and $x=\pm 0.01$. One can see that the differences between two calculations are on the order of a fraction of a percent. We conclude that nonlinear corrections to Eq. (2) can be neglected for all levels considered here.

C. Core-valence correlations

As we mentioned in Sec. I the size of the core-valence correlation corrections *a priori* is not clear. On the one hand

TABLE II. One-configurational calculation of q factors in Dirac-Coulomb, Dirac-Coulomb-Gaunt, and Dirac-Coulomb-Breit approximations (in cm^{-1}); δq_{Gn} and δq_{Br} are respective Gaunt and Breit corrections to Dirac-Coulomb q factors q_{DC}. The latter are calculated for $x=\pm 1/8$ using Eq. (2) and also for $x=\pm 0.01$.

		q_{DC}			
Configuration	Level	$\lvert x\rvert=1/8$	$\lvert x\rvert=0.01$	δq_{Gn}	δq_{Br}
$3d^6 4s$	$^6D_{9/2}$	0.0	0.0	0.0	0.0
$3d^6 4s$	$^6D_{7/2}$	377.0	377.1	−23.2	−23.3
$3d^6 4s$	$^6D_{5/2}$	648.5	648.6	−39.2	−39.3
$3d^6 4s$	$^6D_{3/2}$	833.1	833.2	−49.6	−49.8
$3d^6 4s$	$^6D_{1/2}$	940.7	940.8	−55.6	−55.7
$3d^6 4p$	$^6D^o_{9/2}$	1296.3	1296.4	22.1	18.7
$3d^6 4p$	$^6D^o_{7/2}$	1475.8	1475.9	14.7	11.2
$3d^6 4p$	$^6F^o_{11/2}$	1438.6	1440.8	13.4	10.6
$3d^6 4p$	$^6F^o_{9/2}$	1614.6	1616.9	−0.3	−3.1
$3d^6 4p$	$^6P^o_{7/2}$	1331.8	1333.9	15.7	13.2
$3d^5 4s4p$	$^8P^o_{7/2}$	−2433.6	−2433.8	175.4	156.0
$3d^6 4p$	$^4G^o_{7/2}$	1617.4	1619.9	−55.2	−58.1
$3d^6 4p$	$^4H^o_{7/2}$	1334.5	1336.5	66.9	63.4
$3d^6 4p$	$^4F^o_{7/2}$	1172.5	1173.4	49.8	46.6
$3d^5 4s4p$	$^6P^o_{7/2}$	−1824.7	−1824.9	148.1	130.7

the Ar-like core for Fe II is rather small and rigid. On the other hand valence $3d$ electrons belong to the shell with the same principal quantum number as the outermost core electrons $3s,3p$. Thus, there is no spatial separation between core and valence electrons.

There are two approaches that can be applied to account for core-valence correlations. The first approach is to use the CI+MBPT method [24] and another one is to include two $3s$- and six $3p$-electrons into the valence space. The former method allows using long basis sets and accounting for correlations with all core shells. The main problem with this method is instability of the MBPT for the mean-field potential V^N, which includes a large number of valence electrons, i.e., for $N-N_{\rm core}\gg 1$. At present this method is implemented only for the second order MBPT corrections to valence Hamiltonian. That may be insufficient for accurate treatment of correlations of valence $3d$ electrons with $3s$ and $3p$ electrons from the core. It is known that second-order MBPT usually overestimates core-valence correlations. Potentially more accurate all-order methods, like the one suggested in Ref. [30], are currently used only for the systems with two valence electrons. For example, coupled-cluster calculations of the q factors of a number of divalent atoms and ions was recently reported in Ref. [31].

The latter method is more straightforward, but the problem here is the enormous size of the CI space even for a rather small basis set. Because of that it is impossible to saturate CI, which leads to significant underestimation of the core-valence correlations. Due to these problems neither method can be preferred and we used their combination to estimate corrections caused by core-valence correlations.

We started with solving a seven-electron CI problem for the basis set $[5s4pd]$. Then we solved the 15-electron CI problem using the same basis set and found correction $\delta q_{\rm cv,1}$, which accounted for the correlations between valence electrons and $3s$ and $3p$ electrons from the core. In both cases CI space included SD excitations. The dimension of the CI matrix for the 15-electron problem was on the order of 10^6. That limited the length of the basis set we could use in this approach. Such a short basis set was obviously insufficient for accurate treatment of core-valence correlations. To account for the incompleteness of the basis set we performed two calculations of the q factors using the CI+MBPT method. In one calculation all summations over virtual states in MBPT diagrams ran over the same basis set as above and sums over core states included only $3s$ and $3p$ shells.

Another calculation used a much longer basis set $[21s16p21d19f14g]$ and all core shells. Valence space for both calculations was the same as in the seven-electron CI above. The difference between these two calculations gave us the second correction $\delta q_{\rm cv,2}$, which accounted for correlations with the inner core shells and the incompleteness of the basis set used in the 15-electron CI. The results of these calculations are presented in Table III.

In the 15-electron CI calculation the odd-parity levels $^4G^o_{7/2}$ and $^4H^o_{7/2}$ strongly interacted with each other and their g factors significantly differed from the seven-electron calculation and from the experiment. That hampered the comparison of the respective q factors. We excluded these levels from Table III.

In general CI+MBPT even for a short basis set gave much larger corrections to q factors and to transition frequencies than 15-electron CI. The average discrepancies in the q factors and the transition frequencies for the low-lying odd-parity states are at the levels of 100 and 5500 cm^{-1}, respectively, while for the higher-lying $3d^5 4s4p\ ^6P^o_{7/2}$ state these discrepancies attain 600 and 10 000 cm^{-1}. A comparison of the transition frequencies with the experiment showed

TABLE III. Core-valence corrections to q factors, $\delta q_{cv} = \delta q_{cv,1} + \delta q_{cv,2}$ (in cm^{-1}). The term $\delta q_{cv,1}$ is a difference of 15-electron and seven-electron CI on the basis set $[5s4pd]$. The second term accounts for the incompleteness of this basis set. It is obtained as a difference of seven-electron CI+MBPT on the basis sets $[21s16p21d19f14g]$ and $[5s4pd]$.

Configuration	Level	$\delta q_{cv,1}$	$\delta q_{cv,2}$	δq_{cv}
$3d^64s$	$^6D_{9/2}$	0.0	0.0	0.0
$3d^64s$	$^6D_{7/2}$	10.5	12.3	22.8
$3d^64s$	$^6D_{5/2}$	11.4	25.5	36.9
$3d^64s$	$^6D_{3/2}$	10.5	36.9	47.4
$3d^64s$	$^6D_{1/2}$	8.8	43.0	51.8
$3d^64p$	$^6D^o_{9/2}$	19.3	39.5	58.8
$3d^64p$	$^6D^o_{7/2}$	16.7	19.3	36.0
$3d^64p$	$^6F^o_{11/2}$	17.6	37.7	55.3
$3d^64p$	$^6F^o_{9/2}$	19.3	36.0	55.3
$3d^64p$	$^6P^o_{7/2}$	357.3	36.9	394.2
$3d^54s4p$	$^8P^o_{7/2}$	51.8	99.2	151.0
$3d^64p$	$^4F^o_{7/2}$	240.5	208.1	448.6
$3d^54s4p$	$^6P^o_{7/2}$	69.4	98.3	167.7

that the CI+MBPT method strongly overestimated the core-valence correlations. On the other hand, the 15-electron CI was much closer to the experiment. Because of that we used the CI+MBPT method only to account for the incompleteness of the basis set. Our final estimate of the correction from the core-valence correlation is given by the sum $\delta q_{cv} = \delta q_{cv,1} + \delta q_{cv,2}$.

D. Level $^6P^o_{7/2}$ at 62 172 cm^{-1}

The level $^6P^o_{7/2}$ at 62 172 cm^{-1} is the most important level for the search of α variation. This one is the only level of the configuration $3d^54s4p$, which is observed in astrophysics. All other observed odd-parity levels belong to the configuration $3d^64p$. Note that the ground state belongs to the configuration $3d^64s$. It means that corresponding transitions are of $4s \rightarrow 4p$ type, while transition to the level $^6P^o_{7/2}$ is of $3d \rightarrow 4p$ type. The relativistic corrections increase the binding energy of s electrons and decrease the binding energy of d electrons. Because of that the q factor for the $^6P^o_{7/2}$ level is of the opposite sign to the q factors of all other observed levels. The existence of the q factors of both signs makes the Fe II ion so attractive for the search of α variation.

Initially there was some controversy around this level. In Moore's tables [32] this level was erroneously marked as $3d^6(^7S)4p\,^6P^o_{7/2}$. It was an obvious misprint because there is no term ^7S in configuration $3d^6$, but there is such a term in configuration $3d^54s$. Still, this assignment was used in the first calculation of Fe II [13] for the identification of this level and a positive q factor was obtained. In the next calculation [9] this error was noticed and a negative q factor for this level was reported.

One of the main arguments which allowed us to assign this level to the configuration $3d^54s4p$ was based on the analysis of g factors. The experimental g factor for this level is 1.68 [32,33], while all levels of the configuration $3d^64p$ have significantly smaller g factors. On the other hand, the Landé value of the g factor for the level $^6P_{7/2}$ for the pure LS-coupling scheme is 1.714. The calculated value of the g factor appeared to be very close to the Landé value (see Table I). This was used in Ref. [9] to estimate configuration mixing for this level to be about a few percent and to calculate the corresponding correction to the q factor as follows:

$$\delta q_g \approx +180. \tag{3}$$

Since the publication of the paper [9] the new NIST tables for Fe II became available [33]. These tables confirm assignment of the level $^6P^o_{7/2}$ at 62 172 cm^{-1} to configuration $3d^54s4p$. Moreover, the mixing of the configurations $3d^54s4p$ and $3d^64p$ for this level at a few percent was also independently confirmed from the analysis of the branching ratios [34]. Therefore, we conclude that application of the correction (3) is justified. The correction of the opposite sign has to be applied to the closest interacting level $^4F^o_{7/2}$.

At present it is impossible to reproduce this configurational mixing in the *ab initio* calculations because it is very sensitive to the relative position of the levels. The nondiagonal matrix elements which cause this mixing are very small, on the order of 10 cm^{-1}, and mixing takes place only when the splitting between interacting levels is about 100 cm^{-1} or less. However, the accuracy of the present theory is insufficient to reproduce the energy intervals between the levels of different configurations with such accuracy (see Table I). Because of that we still have to introduce correction (3) semiempirically. If more accurate experimental data on g factors and the branching ratios becomes available they may help to refine this analysis.

IV. CONCLUSIONS

Our final results for the q factors of the astrophysically important levels of the Fe II ion are given in Table IV. In addition to the large-scale seven-electron CI calculation for the Dirac-Coulomb "no pair" Hamiltonian, we calculated corrections due to the Breit interaction and core-valence correlations. Both corrections appeared to be larger than was anticipated in the previous calculation [9]. Nevertheless our calculations confirm the previous conclusion that the q factors of the levels of the configuration $3d^64p$ are large and positive, while the state $^6P^o_{7/2}$ at 62 172 cm^{-1} belongs to the configuration $3d^54s4p$ and has a large negative q factor.

We found out that the Breit interaction between valence electrons is of the same order of magnitude as the core-valence Breit interaction. Methods accounting for MBPT corrections developed so far do not allow us to treat core-valence correlations accurately for such complicated systems as Fe II. Besides, we were unable to reproduce in the frame of the CI method strong mixing between the level $^6P^o_{7/2}$ of configuration $3d^54s4p$ and nearly located levels of configuration $3d^64p$. Corrections to q factors due to this mixing were found semiempirically using g factor analysis [9]. This analysis is qualitatively confirmed by the analysis of the branching ratios [34]. Considering the two problems men-

TABLE IV. Recommended values for q factors in respect to the ground state, $q_{\mathrm{rec}}=q_{\mathrm{val}}+\delta q_{\mathrm{Br}}+\delta q_{\mathrm{cv}}+\delta q_g$, with uncertainties in parentheses (in cm^{-1}). Valence contribution q_{val} corresponds to the longest basis set $[7spdf]$ from Table I. Breit correction δq_{Br} and core-valence correlation correction δq_{cv} are taken from Tables II and III. Finally, a g factor correction δq_g is given by Eq. (3).

						q_{rec}	
Configuration	Level	q_{val}	δq_{Br}	δq_{cv}	δq_g	This work	Ref. [9]
$3d^64p$	$^6D^o_{9/2}$	1334	19	59	0	1410 (60)	1330 (150)
$3d^64p$	$^6D^o_{7/2}$	1488	11	36	0	1540 (40)	1490 (150)
$3d^64p$	$^6F^o_{11/2}$	1479	11	55	0	1550 (60)	1460 (150)
$3d^64p$	$^6F^o_{9/2}$	1607	−3	55	0	1660 (60)	1590 (150)
$3d^64p$	$^6P^o_{7/2}$	1134	13	394	0	1540 (400)	1210 (150)
$3d^64p$	$^4F^o_{7/2}$	1240	47	449	−180	1560 (500)	1100 (300)
$3d^54s4p$	$^6P^o_{7/2}$	−1506	131	168	180	−1030 (300)	−1300 (300)

tioned above as a main source of uncertainties we can roughly estimate the final uncertainties Δ of the q factors presented in Table IV as

$$\Delta \simeq \sqrt{(\delta q_{\mathrm{cv}})^2 + (\delta q_g)^2}.$$

As is seen from Table IV the uncertainties for the q factors for the low-lying astrophysically important states are at the level of 4% while for higher-lying levels they attain 30%. Further development of the CI+MBPT method allowing one to treat core-valence correlations more accurately and the appearance of more precise experimental data on g factors and transition rates for these levels would be very helpful in improving the accuracy of the q factors.

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