Relativistic corrections to the isotope shift in light ions

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(Received 26 February 2007; published 17 August 2007)

We calculate the isotope mass shift for several light atoms and ions using Dirac wave functions and the mass shift operator with relativistic corrections of the order of $(\alpha Z)^2$. Calculated relativistic corrections to the specific mass shift vary from a fraction of a percent for carbon to 2% for magnesium. Relativistic corrections to the normal mass shift are typically smaller. Interestingly, the final relativistic mass shifts for the levels of one multiplet appear to be even closer to each other than for nonrelativistic operators applied to Dirac functions. That can be important for the astrophysical search for possible α variation, where the isotope shift is a source of important systematic error. Our calculations show that for levels of the same multiplet this systematics is negligible, and they can be used as probes for α variation.

DOI: 10.1103/PhysRevA.76.022103 PACS number(s): 06.20.Jr, 31.30.Gs, 31.25.Jf

I. INTRODUCTION

Modern theories (such as string theory and M theory) predict temporal and spatial variations of fundamental physical constants. Some recent studies of quasar absorbtion spectra indicate that the fine-structure constant $\alpha=e^2/\hbar c$, where e is the charge of the electron and $\hbar$ and c are the reduced Planck constant and the speed of light, respectively, could have changed during the evolution of the Universe (see [1] and references therein). This result was not confirmed by other groups [2–6], and hence new experiments are required. Laboratory experiments are rapidly increasing their sensitivity to α variation (see [7,8] and references therein), but are currently slightly less sensitive than astrophysical ones, where the time scale is 10^{10} times longer. Finally, there may be some evidence for varying α from the natural nuclear reactor in Oklo, which operated about 2 billion years ago [9].

Astrophysical studies are based on the fact that atomic transition frequencies depend on the parameter $x=(\alpha/\alpha_0)^2-1$, where $\alpha_0\approx 1/137$ is the laboratory value of α. Thus, one can look for α variation by comparing the frequencies of atomic lines in the spectra of quasars with their laboratory values, which correspond to $x=0$. One of the major systematic effects, which can imitate α variation, is the isotope shift (IS). It had been shown previously [10–13] that the typical IS is of the same order of magnitude as the effect observed in [1].

In [14], a method to separate the effect of varying α from the IS was proposed. This method is based on building special combinations of atomic frequencies, some of which are insensitive to both effects ("anchors"), while the others are independent of the IS, but sensitive to α variations ("probes"). One could then use the anchors to retrieve the actual value of the redshift of the spectrum, and then use the probes to evaluate the size of the variation $\Delta\alpha/\alpha$. In addition, one can form probes that are sensitive to the IS, but not to the variation of α. These probes could provide information about isotopic abundances in the early Universe. Such information should also be of interest to the astrophysicists, because isotopic evolution is tightly linked with the general evolution of the Universe.

The described method of anchors and probes requires precise calculations of atomic relativistic coefficients q, which determine the dependence of the transition frequencies on x, and the IS coefficients $k_{\rm IS}$. The factors q strongly depend on the total angular momentum J, which distinguishes levels of the same multiplet. Relativistic corrections to the coefficients $k_{\rm IS}$ are known to be small and their dependence on J is much weaker. Nevertheless, in order to separate the two effects reliably, one needs to accurately account for relativistic corrections to the IS. For light atoms the IS is dominated by the mass shift (MS). Usually MS calculations are done with Dirac wave functions, but using a nonrelativistic form of the MS operator. In this paper we report results of MS calculations for 12 light atoms and ions. We use a MS operator that includes relativistic corrections of the order of $(\alpha Z)^2$ [15–17]. It is shown that relativistic corrections to the operator partly compensate corrections to the wave functions, and the final relativistic corrections are smaller than in previous calculations. That may help to distinguish between α variation and isotope effects in astrophysics.

II. METHOD

A. Theory of isotope shift

The total IS consists of the MS and the field shift (FS). The former accounts for the finite mass of the nucleus, and the latter accounts for the finite size of the nucleus. In the nonrelativistic theory the MS is further divided into the normal mass shift (NMS) and the specific mass shift (SMS). The overall IS in the frequency of any atomic transition of an isotope with mass number A' with respect to an isotope with mass number A can be written as (see, for example, [18])

$$\delta\nu^{A',A}=(k_{\rm NMS}+k_{\rm SMS})\left(\frac{1}{A'}-\frac{1}{A}\right)+F\delta\langle r^2\rangle^{A',A}, \qquad (1)$$

where $\langle r^2\rangle$ is the nuclear mean square radius, F is the FS coefficient, and $k_{\rm MS}=k_{\rm NMS}+k_{\rm SMS}$ is the MS coefficient. In the nonrelativistic theory the NMS is described by the one-electron operator,

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$$H_{\mathrm{NMS}}^{(\mathrm{nr})} = \frac{1}{2M}\sum_i \boldsymbol{p}_i^2, \tag{2}$$

where $\boldsymbol{p}_i$ is the momentum of the ith electron. Because of the virial theorem, k_{NMS} has the simple form

$$k_{\mathrm{NMS}}^{(\mathrm{nr})} = -\frac{\omega}{1823}, \tag{3}$$

where the number 1823 refers to the ratio of the atomic mass unit (amu) to the electron mass. The SMS is described by a two-electron operator

$$H_{\mathrm{SMS}}^{(\mathrm{nr})} = \frac{1}{M}\sum_{i<k} \boldsymbol{p}_i \cdot \boldsymbol{p}_k. \tag{4}$$

A consistent relativistic theory of the MS can be formulated only within quantum electrodynamics in the form of an expansion in αZ. It was shown in Refs. [15–17] that the first two terms of the expansion in αZ lead to the following relativistic MS Hamiltonian:

$$H_{\mathrm{MS}}^{(\mathrm{r})} = \frac{1}{2M}\sum_{i,j}\left(\boldsymbol{p}_i\boldsymbol{p}_j - \frac{\alpha Z}{r_i}[\boldsymbol{\alpha}_i + (\boldsymbol{\alpha}_i\hat{\boldsymbol{r}}_i)\hat{\boldsymbol{r}}_i]\boldsymbol{p}_j\right), \tag{5}$$

where $\boldsymbol{\alpha}_i$ is the Dirac matrix of the ith electron and $\hat{\boldsymbol{r}}=\boldsymbol{r}/r$. As in the nonrelativistic theory, one can divide the Hamiltonian (5) into the one- and two-electron terms

$$H_{\mathrm{NMS}} = \frac{1}{2M}\sum_i \left(\boldsymbol{p} - \frac{\alpha Z}{2r}[\boldsymbol{\alpha} + (\boldsymbol{\alpha}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}]\right)_i^2, \tag{6}$$

$$H_{\mathrm{SMS}} = \frac{1}{M}\sum_{i<k}\left(\boldsymbol{p} - \frac{\alpha Z}{2r}[\boldsymbol{\alpha} + (\boldsymbol{\alpha}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}]\right)_i \times\left(\boldsymbol{p} - \frac{\alpha Z}{2r}[\boldsymbol{\alpha} + (\boldsymbol{\alpha}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}]\right)_k. \tag{7}$$

The nonrelativistic expression (3) is not applicable to the operator (6) and now k_{NMS} has to be calculated on the same footing as k_{SMS}.

As pointed out above, for light atoms and ions the FS is much smaller than the MS. Still, for comparison with high-precision experiments one may need to account for the FS. Below we focus on calculating the MS, but in the final Table V we present FS factors for some of the transitions.

B. Electron correlations

The IS is very sensitive to electron correlations. High-accuracy calculations must account not only for correlations between valence electrons, but also for core-valence correlations. Here we treat both types of correlation within configuration interaction (CI)+ many-body perturbation theory (MBPT) method [19]. In this method the configuration-interaction calculation is done for valence electrons using the effective Hamiltonian H_{eff}, which is formed within the second-order many-body perturbation theory in the residual core-valence interaction. All our calculations are done with the modified Dirac-Fock code [20], CI code [21], and MBPT code [19].

The CI+MBPT method is easily reformulated for IS calculations within the finite-field approximation. In this approximation, the IS operator H_{IS} is added to the many-particle Hamiltonian H with an arbitrary coefficient λ:

$$H_\lambda = H + \lambda H_{\mathrm{IS}}. \tag{8}$$

The eigenvalue problem for Hamiltonian (8) is solved for $+\lambda$ and for $-\lambda$. Then, the IS correction to the energy is recovered as

$$\Delta E_{\mathrm{IS}} = \frac{E_{+\lambda} - E_{-\lambda}}{2\lambda}. \tag{9}$$

All calculations are done independently for the field, normal, and specific parts of the IS. The parameter λ is chosen from considerations of the numerical stability and smallness of the nonlinear terms. In the CI+MBPT calculations, the Hamiltonian (8) is used to construct $H_{\lambda,\mathrm{eff}}$. That means that H_λ is used in all stages of calculation starting from solving the Dirac-Fock equations for the atomic core.

The CI+MBPT method provides the solution of the eigenvalue problem for valence electrons $H_{\mathrm{eff}}\Psi = E\Psi$, which is an approximation to the all-electron problem $H\Psi = E\Psi$. The latter equation gives an exact solution for the given basis set. Unfortunately, this equation can be solved only for atoms with few electrons and only for very short basis sets. Nevertheless, on a short basis set we can compare all-electron and CI+MBPT calculations with some simple calculations (for example, with the one-configurational approximation) and designate corresponding corrections as Δ^{short} and $\Delta_{\mathrm{eff}}^{\mathrm{short}}$. Then we repeat the CI+MBPT calculation on a much longer basis set and find a new correction $\Delta_{\mathrm{eff}}^{\mathrm{long}}$. Although we cannot make an all-electron calculation for the long basis set, we can use the short-basis-set calculation to shift the central point of the final CI+MBPT calculation and estimate its error:

$$\delta_{\mathrm{shift}} \approx \Delta^{\mathrm{short}} - \Delta_{\mathrm{eff}}^{\mathrm{short}}, \tag{10}$$

$$\delta_{\mathrm{err}} \approx \delta_{\mathrm{shift}}\frac{\Delta_{\mathrm{eff}}^{\mathrm{long}}}{\Delta_{\mathrm{eff}}^{\mathrm{short}}}. \tag{11}$$

We will use Eq. (10) where possible to improve the CI+MBPT results and Eq. (11) to estimate the theoretical error.

All basis sets mentioned in this paper are constructed by adding a certain number of B splines to the numerical Dirac-Fock orbitals and diagonalizing the Dirac-Fock Hamiltonian. For many-electron atoms, the size of the CI space strongly depends on the basis set. Usually MBPT calculations of core-valence correlations require much longer basis sets than the valence CI. The CI+MBPT method allows use of different basis sets for CI and MBPT parts of the calculation [22], so we usually form two different basis sets for each atom. The shorter CI basis set is generated independently and is not a subset of the longer basis set for MBPT.

III. RESULTS OF THE CALCULATIONS

A. Lithiumlike ions

Lithium is the simplest atom in our consideration, since it has only one core orbital $1s$ and one valence electron. The

TABLE I. Isotope shifts (in MHz) in the spectrum of ^{6}Li, with respect to ^{7}Li. In the second column the result of our CI+MBPT calculation is given. The third column presents corrected values using Eq. (10) and the errors are estimated with the help of Eq. (11).

	Theory		
Transition	CI+MBPT	Corrected	Expt.
$2s_{1/2} \to 2p_{1/2}$	10346	10608(300)	10534.26(13)[a]
			10532.9(6)[b]
			10534.3(3)[c]
			10533.13(15)[d]
$2s_{1/2} \to 2p_{3/2}$	10346	10607(300)	10533.3(5)[b]
			10539.9(1.2)[c]
			10534.93(15)[d]
$2s_{1/2} \to 3p_{1/2}$	14162	14380(250)	14470(450)[e]
$2s_{1/2} \to 3p_{3/2}$	14162	14380(250)	14470(450)[e]
$2s_{1/2} \to 3d_{3/2}$	13194	13402(250)	13314(6)[f]
			13312(4)[g]
$2s_{1/2} \to 3d_{5/2}$	13194	13402(250)	13314(6)[f]
			13312(4)[g]
$2s_{1/2} \to 4s_{1/2}$	14565	14747(200)	14656(6)[f]
			14661(14)[g]

[a]Reference [23].
[b]Reference [24].
[c]Reference [25].
[d]Reference [26].
[e]Reference [27].
[f]Reference [28].
[g]Reference [29].

simplicity of this system allows one to perform all-electron (full) CI calculations for all three electrons. This calculation provides an exact solution on a given one-electron basis set and allows us to improve our results and to control their accuracy using Eqs. (10) and (11). The basis set consists of the orbitals: $1s$–$9s$, $2p$–$9p$, $3d$–$8d$, and $4f$–$8f$ (basis set $[9sp8df]$). The CI+MBPT calculation is then done with two longer basis sets: the valence CI space is defined by the basis set $[13sp12df]$ and all intermediate MBPT summations run over the basis set $[17sp18d19f20g21h]$. In Table I we compare our MS calculations with the experiment. For Li the relative size of the FS is about 10^{-5} and we neglect it.

We see that most experimental results for IS in Li are much more accurate than our calculations. Corrections (10) lead to significant improvement of the agreement between calculations and experiment. The error estimate (11) appears to be quite reliable here as most calculated CI+MBPT values and all corrected values agree with experimental data within the estimated errors. We conclude that Eqs. (10) and (11) work nicely for lithium. On the other hand, even for such a simple system as Li, our theoretical error for MS appears to be about 2%, while the typical error for the frequencies is only about 0.1%. That shows the extreme sensitivity of the MS to correlations and significantly more important role of the high order MBPT corrections, which are neglected here.

Calculations of other Li-like ions are done in a similar way using basis sets of the same length. Corresponding results for C IV, N V, and O VI are given in the final Table V. There we also use Eq. (11) to estimate theoretical accuracy.

TABLE II. Isotope shifts (in MHz) for ^{11}B with respect to ^{10}B in the spectrum of B II.

		IS	
Transition	λ (Å)	Theory	Expt.
$^1S_0[2s^2] \to {}^1P^o_1[2s2p]$	1362	21303(66)	21000(3000)[a]
			21000(3000)[b]
$^3P^o_1[2s2p] \to {}^3P_2[2p^2]$	1624	22367(170)	21600(3600)[a]
			24000(3600)[b]
$^3P^o_0[2s2p] \to {}^3P_1[2p^2]$	1624	22369(170)	21600(3600)[a]
			21600(3600)[b]
$^3P^o_1[2s2p] \to {}^3P_1[2p^2]$	1624	22370(170)	21600(6900)[a]
			21600(6900)[b]
$^3P^o_2[2s2p] \to {}^2P_2[2p^2]$	1624	22369(170)	21600(4500)[a]
			18300(4500)[b]
$^3P^o_1[2s2p] \to {}^3P_0[2p^2]$	1624	22371(170)	21600(3600)[a]
			21600(3600)[b]
$^3P^o_2[2s2p] \to {}^3P_1[2p^2]$	1624	22372(170)	21600(3600)[a]
			21600(3600)[b]
$^1P^o_1[2s2p] \to {}^1S_0[2p^2]$	1843	12689(580)	12600(1200)[b]
$^1P^o_1[2s2p] \to {}^1D_2[2p^2]$	3451	26663(55)	26600(100) [b]
			26300(120)[c]

[a]Reference [30].
[b]Reference [31].
[c]Reference [32].

B. B II, C III, and C II

We treat Be-like ions B II and C III as two-electron ions with $1s^2$ core and the ground state $^1S_0[2s^2]$. Since the full 4-electron CI calculation is more complex than in the case of 3-electron Li, a shorter basis set $[5sp4df]$ is used here for such calculation. Valence two-electron CI calculations were done with $[10sp9df]$ and MBPT corrections were calculated using the $[16sp17d18f19g20h]$ basis set.

There are many experimental results for B II. Table II presents the comparison of calculated and experimental ISs for B II. Unlike the case of lithium, here for most transitions the estimated theoretical error is smaller than the experimental one. We see that generally there is good agreement between theory and experiment. Our calculation of the IS in the transition $^1P^o_1 \to {}^1D_2$ is in good agreement with the measurement [30], but is 3σ away from the result of Ref. [31]. Note that for the transition $^1P^o_1 \to {}^1S_0$ the MBPT correction for the long basis set appears to be anomalously large. That leads to the much larger theoretical error than for other transitions.

C II is the only B-like ion that is interesting for astrophysics. It is also of a particular interest to us because the experiment [33] hints at approximately 2% difference between the shifts for the relativistic doublet. If this is confirmed, it will mean that relativistic corrections to the IS are quite large even for light ions and should be included in accurate calculations. That will also make isotope effects more dangerous for the astrophysical searches for α variation.

The ground state of C II is $^2P^o_{1/2}[2s^22p_{1/2}]$. It has five electrons and full CI calculation becomes impractical even for the short basis set. That makes it more difficult to determine

TABLE III. IS for ^{13}C with respect to ^{12}C in the doublet line $^2S_{1/2}[2s2p^2] \rightarrow {}^2P^o_J[2s^23p]$ of C II. Here we use relativistic MS operators (6) and (7). The calculation of Berengut *et al.* [34] was done with nonrelativistic operators.

Transition	λ (Å)	IS (MHz) This work	IS (MHz) Theory [34]	IS (MHz) Expt. [33]
$^2S_{1/2} \rightarrow {}^2P^o_{3/2}$	2836.707	−18185.0	−18500	−18350(60)
$^2S_{1/2} \rightarrow {}^2P^o_{1/2}$	2837.605	−18185.9	−18500	−18680(90)

the theoretical error. Using our calculations for Li-like and Be-like ions, we estimate the theoretical error for C II to be about 1–2 %. On the other hand, with relativistic MS operators (6) and (7) the relative size of the shifts within one multiplet should be also accurate to few percent. Our results shown in Table III indicate that the difference between the shifts in this doublet must be roughly two orders of magnitude smaller than hinted by the experiment [33]. In fact, as we discuss below in more detail, using the relativistic operator (5) brings the MS shifts for the levels of one multiplet closer to each other than with nonrelativistic operators (2) and (4).

C. Sodiumlike ions and Mg I

There are several Na-like ions which are important for astrophysics, namely, Na I, Mg II, Al III, and Si IV. For Na I and Mg II there are experimental data available and we compare the calculated MS with the experiment in Table IV. Using nuclear radii from Ref. [44] we have estimated the FS for $3s \rightarrow 3p$ transitions in $^{22-23}$Na I and $^{24-26}$Mg II to be about −2 and +16 MHz, respectively. This is significantly smaller than the uncertainty in our MS calculation.

In these calculations for Na I, Al III, and Si IV we use the CI basis set $[14sp13df]$ and the MBPT basis set $[19sp18d19f20g21h]$. Our IS results for Si IV are within 1% agreement with the calculation of Berengut *et al.* [45], while the differences for Mg I are larger and can reach several percent.

Neutral magnesium is one of the most well studied two-electron atoms. The data from several experimental works on the IS in Mg I, II are presented in Table IV and compared with the theoretical IS calculated on the basis sets $[12spd9f]$ and $[17spdf9gh]$.

IV. DISCUSSION

Our final results for the MS in astrophysically important transitions are listed in Table V. Where available we also give FS parameters and results of other calculations of the SMS and relativistic q factors. The latter are known to be significantly different for the lines of one multiplet because the splittings within the multiplet are caused by relativistic spin-orbit interaction and scale as $(\alpha Z)^2$. That makes these splittings natural candidates as probes for α variation. However, the J dependence of the IS may introduce some systematic errors as isotope abundances in the Universe may vary significantly. Here we use relativistic MS operators and show

TABLE IV. Comparison with experiment for IS in Na I and Mg I. The FS is neglected (see text). All numbers are in MHz.

Transition	λ (Å)	MS	IS (expt.)
$^{22-23}$Na I			
$3s \rightarrow 3p_{1/2}$	5896	775.8	758.5(7)[a]
			756.9(1.9)[b]
$3s \rightarrow 3p_{3/2}$	5890	776.5	757.72(24)[c]
$^{24-26}$Mg II			
$3s \rightarrow 3p_{3/2}$	2796	3086.3	3050(100)[d]
$^{24-26}$Mg I			
$^1S_0[3s^2] \rightarrow {}^3P^o_1[3s3p]$	4571	2686.9	2683.2(0)[e]
$^1S_0[3s^2] \rightarrow {}^1P^o_1[3s3p]$	2852	1425.3	1415.3(5.0)[f]
$^3P^o_0[3s3p] \rightarrow {}^3S_1[3s4s]$	5167	−367.9	−395.7(6.0)[g]
$^3P^o_1[3s3p] \rightarrow {}^3S_1[3s4s]$	5173	−369.9	−391.2(4.5)[g]
$^3P^o_2[3s3p] \rightarrow {}^3S_1[3s4s]$	5184	−373.1	−392.7(7.5)[g]
$^3P^o_1[3s3p] \rightarrow {}^3D_2[3s3d]$	3832	58.7	60.6(3.0)[h]
$^3P^o_2[3s3p] \rightarrow {}^3D_3[3s3d]$	3838	55.8	58.2(3.6)[h]
$^1S_0[3s^2] \rightarrow {}^1P^o_1[3s4p]$	2026	2975.0	2918.9(1.2)[i]
$^{24-25}$Mg I			
$^1S_0[3s^2] \rightarrow {}^3P^o_1[3s3p]$	4571	1397.2	1405.2(0.1)[e]
$^1S_0[3s^2] \rightarrow {}^1P^o_1[3s3p]$	2852	741.2	743.8(3.0)[f]
$^3P^o_2[3s3p] \rightarrow {}^3S_1[3s4s]$	5184	−194.0	−203.9(7.5)[g]
$^1S_0[3s^2] \rightarrow {}^1P^o_1[3s4p]$	2026	1547.0	1526.4(1.2)[i]

[a]Reference [35].
[b]Reference [36].
[c]Reference [37].
[d]Reference [38].
[e]Reference [39].
[f]Reference [40].
[g]Reference [41].
[h]Reference [42].
[i]Reference [43].

that the J dependence for the MS is smaller than one might expect from the simple considerations and from experiment [33]. That means that multiplet splittings are indeed good probes for α variation.

In several cases we also made SMS calculations using the nonrelativistic operator (4) (see Table V). Comparison with our relativistic values indicates that relativistic corrections grow from a fraction of a percent for carbon ions to about 1–2 % for Mg I, II. It is interesting though, that relativistic MS values for one multiplet tend to be closer to each other than nonrelativistic values. The difference between final MS shifts within one multiplet appears to be much smaller than the relativistic corrections themselves. It should be mentioned that the nonrelativistic SMS presented in Table V was obtained by applying the operator (4) only to the upper components of the Dirac functions. If this operator is applied to both components, the result tends to be noticeably farther from the correct relativistic value [52]. Most of the previous calculations cited in Table V applied the nonrelativistic SMS operator to Dirac-Fock orbitals. The only exception is the

TABLE V. Isotope shift parameters for astrophysically important transitions in Li-, Be-, B-, and Na-like ions, and in Mg I. The experimental values for the transition wavelengths were taken from the NIST atomic spectra database [46]. The SMS and NMS parameters are given in GHz amu, the FS parameter F is given in MHz/fm^2. Nonrelativistic values for k_{SMS} and k_{NMS} were obtained with operator (4) and scaling (3), respectively.

		k_{SMS}			k_{NMS}			
Transition	λ (Å)	Nonrelativistic	Relativistic	Other works	Nonrelativistic	Relativistic	F	q
			C IV					
$2s_{1/2}\rightarrow 2p_{1/2}$	1551	−4509	−4497(45)	−4511(23)[a] −4527[c]	−1060.5	−1061.1	−174	104[b]
$2s_{1/2}\rightarrow 2p_{3/2}$	1548	−4502	−4499(45)	−4504(23)[a] 4527[c]	−1062.3	−1061.2	−173	232[b]
			C III					
$^1S_0[2s^2]\rightarrow {}^3P^o_0[2s2p]$	1910	−3461	−3453(7)	−3473[a]	−861.3	−860.3		74[a]
$^1S_0[2s^2]\rightarrow {}^3P^o_1[2s2p]$	1909	−3459	−3454(7)	−3472[a]	−861.6	−860.2		108[a]
$^1S_0[2s^2]\rightarrow {}^3P^o_2[2s2p]$	1907	−3456	−3454(7)	−3468[a]	−862.6	−860.1		178[a]
$^1S_0[2s^2]\rightarrow {}^1P^o_1[2s2p]$	977	−2778	−2774(80)	−2790[a]	−1683.3	−1677.3		165[a]
			C II					
$^2P^o_{1/2}[2s^22p]\rightarrow {}^2S_{1/2}[2s2p^2]$	1036		−1295	−1321[a]	−1586.9	−1591.1		168[a]
$^2P^o_{1/2}[2s^22p]\rightarrow {}^2D_{3/2}[2s2p^2]$	1335		−2636	−2671[a]	−1232.3	−1230.3		178[a]
$^2P^o_{1/2}[2s^22p]\rightarrow {}^2D_{5/2}[2s2p^2]$	1334		−2637	−2672[a]	−1232.3	−1230.4		181[a]
$^2P^o_{1/2}[2s^22p]\rightarrow {}^4P_{1/2}[2s2p^2]$	2325		−2971	−2960[a]	−707.2	−700.7		132[a]
$^2P^o_{1/2}[2s^22p]\rightarrow {}^4P_{3/2}[2s2p^2]$	2324		−2972	−2958[a]	−707.6	−700.7		158[a]
$^2P^o_{1/2}[2s^22p]\rightarrow {}^4P_{5/2}[2s2p^2]$	2322		−2973	−2956[a]	−708.1	−700.6		202[a]
			N V					
$2s_{1/2}\rightarrow 2p_{1/2}$	1243	−7123	−7099(70)	−7137[c]	−1323.3	−1324.7	−417	196[d]
$2s_{1/2}\rightarrow 2p_{3/2}$	1239	−7109	−7103(70)	−7137[c]	−1327.6	−1325.7	−386	488[d]
			O VI					
$2s_{1/2}\rightarrow 2p_{1/2}$	1038	−10312	−10266(100)	−10315[c]	−1585.0	−1587.0	−719	340[b]
$2s_{1/2}\rightarrow 2p_{3/2}$	1032	−10283	−10273(100)	−10315[d]	−1593.7	−1590.5	−719	872[b]
			Na I					
$3s_{1/2}\rightarrow 3p_{1/2}$	5896		−116	−108(24)[e] −97[f]	−278.9	−278.3	−33	45[b]
$3s_{1/2}\rightarrow 3p_{3/2}$	5890		−116	−107(24)[e] −97[f]	−279.2	−278.5	−33	63[b]
			Mg II					
$3s_{1/2}\rightarrow 3p_{1/2}$	2803	−387	−378	−373(12)[e] −362[f]	−586.6	−585.6	−127	120[d]
$3s_{1/2}\rightarrow 3p_{3/2}$	2796	−381	−378	−373(6)[e] −361[f]	−588.1	−586.3	−127	211[d]

TABLE V. (*Continued.*)

Transition	λ (Å)	k_{SMS} Nonrelativistic	k_{SMS} Relativistic	k_{SMS} Other works	k_{NMS} Nonrelativistic	k_{NMS} Relativistic	F	q
			Mg I					
$^1S_0[3s^2]\rightarrow{}^1P_1^o[3s4p]$	2026	−102	−101	−108[g]	−811.6	−816.9	−175	87[g]
$^1S_0[3s^2]\rightarrow{}^1P_1^o[3s3p]$	2852	129	130	134[g]	−576.5	−575.3	−175	94[g]
			Al III					
$3s_{1/2}\rightarrow 3p_{1/2}$	1863		−835		−882.9	−882.6	−254	216[d]
$3s_{1/2}\rightarrow 3p_{3/2}$	1855		−834		−886.7	−884.6	−254	464[d]
			Si IV					
$3s_{1/2}\rightarrow 3p_{1/2}$	1403		−1510	−1535(11)[e]	−1172.4	−1171.1	−497	362[d]
$3s_{1/2}\rightarrow 3p_{3/2}$	1394		−1507	−1505(7)[e]	−1180.0	−1175.6	−480	766[d]

[a]Reference [34].
[b]Reference [47].
[c]Reference [48] (nonrelativistic calculation).
[d]Reference [49].
[e]Reference [45].
[f]Reference [50].
[g]Reference [51].

calculation of Godefroid *et al.* [48], where the nonrelativistic multiconfiguration Hartree-Fock method was used.

It should be mentioned that relativistic calculations of the NMS require special care. Indeed, even in the nonrelativistic limit, the calculated NMS will correspond to the scaling (3) for the theoretical rather then experimental frequency. For light many-electron atoms the difference between experimental and calculated frequencies can be larger than the actual relativistic effects. To account for that one can multiply the calculated relativistic NMS by the ratio $\omega_{expt}/\omega_{theor}$. The values presented in Table V include this correction.

Using q factors from Table V we can also form a number of probes for isotope abundances, which are insensitive to α variations. There are several such probes for carbon ions. The following probe for C IV:

$$P_1^{IS} = 0.69\omega(2s_{1/2}\rightarrow 2p_{1/2})_{C\ IV} - 0.31\omega(2s_{1/2}\rightarrow 2p_{3/2})_{C\ IV} = 24\,470.71\ \text{cm}^{-1}, \quad (12)$$

has the MS parameter $k_{MS}=2112$ GHz amu. More probes can be constructed from C III lines:

$$P_2^{IS} = 0.71\omega(^1S_0\rightarrow{}^3P_0^o)_{C\ III} - 0.29\omega(^1S_0\rightarrow{}^3P_2^o)_{C\ III} = 21\,970.95\ \text{cm}^{-1}, \quad (13)$$

$$P_3^{IS} = 0.59\omega(^1S_0\rightarrow{}^3P_0^o)_{C\ III} - 0.41\omega(^1S_0\rightarrow{}^3P_1^o)_{C\ III} = 9416.36\ \text{cm}^{-1}, \quad (14)$$

$$P_4^{IS} = 0.69\omega(^1S_0\rightarrow{}^3P_0^o)_{C\ III} - 0.31\omega(^1S_0\rightarrow{}^1P_1^o)_{C\ III} = 4404.14\ \text{cm}^{-1}. \quad (15)$$

These probes have $k_{MS}=1810$, 776, and 1593 GHz amu, respectively. Finally, one can form two probes for Li-like nitrogen and oxygen:

$$P_5^{IS} = 0.71\omega(2s_{1/2}\rightarrow 2p_{1/2})_{N\ V} - 0.29\omega(2s_{1/2}\rightarrow 2p_{3/2})_{N\ V} = 33\,719.52\ \text{cm}^{-1}\ (k_{MS}=3537\ \text{GHz amu}), \quad (16)$$

$$P_6^{IS} = 0.72\omega(2s_{1/2}\rightarrow 2p_{1/2})_{O\ VI} - 0.28\omega(2s_{1/2}\rightarrow 2p_{3/2})_{O\ VI} = 42\,255.9\ \text{cm}^{-1}\ (k_{MS}=5213\ \text{GHz amu}). \quad (17)$$

V. CONCLUSIONS

We have used the method of the effective Hamiltonian to calculate the IS for astrophysically important transitions in ions with several valence electrons. We used relativistic MS operators and found that relativistic corrections for light atoms and ions are not suppressed numerically and are of the order of $(\alpha Z)^2$, i.e., 1% for $Z\approx 10$. However, these corrections appear to be very close to each other for the levels of a given multiplet. As a result, the difference between MS values within one multiplet is at least one order of magnitude smaller than the corresponding relativistic corrections.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, Grant No. 05-02-16914. V.K. also acknowledges support from the St. Petersburg government, Grant No. M06-2.4D-220, and grants of the Dynasty Foundation and the Alferov Fund.

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