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Relativistic frequency shifts in Cr, Ti, Fe, Ni, Ca, Na, and V to search for variations in the fine-structure constant

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Sensitivity of the frequencies of 22 atomic transitions to the variation of the fine-structure constant α is calculated. The findings are to be used in a search for possible variations of α across our galaxy using high-quality spectroscopic data for stars similar to our sun.

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I. INTRODUCTION

Theories unifying particle physics and cosmology predict possible variation of the fundamental constants in space and time. Values of these constants may depend on a cosmological scalar field representing dark energy or dark matter [1–5].

Many searches for variations in the low-energy value of the fine-structure constant, $\alpha \equiv e^2/\hbar c$, rely on understanding the sensitivity of atomic transtion frequencies on α (e.g., [6,7]). Indeed, these were recently calculated for 13 transitions seen in infrared stellar spectra and used to probe for differences between α in giant stars near the Galactic Center and the laboratory value [8]. This is also required for a new probe of α variation across our galaxy, using stars very similar to our sun, called "solar twins" [9–11]. This star-to-star comparison largely avoids systematic errors in the usual star-to-laboratory approach, particularly effective shifts and asymmetries in absorption lines from several physical processes as they arise in stellar atmospheres.

The solar twins approach seeks to take advantage of the richness of optical stellar spectra, with potentially hundreds of strong (but unsaturated) absorption lines available, in principle, for comparison between stars to measure any differences in α. However, in practice, there are many reasons to carefully select only transitions which are likely to be most reliable [11]. In particular, using closely separated pairs of transitions, which have very similar strengths in solar twin spectra, suppresses many systematic errors of instrumental and astrophysical origin. To use the thousands of high-quality archival stellar spectra available from the High-Accuracy Radial Velocity Planetary Searcher spectrograph [12] on the European Southern Observatory's 3.6-m telescope at La Silla Observatory (Chile), 164 different transitions were selected, which form 229 close pairs [11]. However, the sensitivity of these transitions to variations in α have not been calculated before. Here we calculate sensitivities for 22 of these transitions, forming 17 pairs, which have been used to compare α between 18 solar twins in [9,10].

II. CALCULATIONS

The dependence of atomic transition frequencies on the fine-structure constant α was studied before for a number of systems (see, e.g., [6,7]). In particular, Ti and Fe were considered in Refs. [13,14]. However, in the present work we use atomic transitions which were never considered before. To perform the calculations we use similar approaches as before accompanied with a method for atoms with complicated electronic structure (many electrons in open shells). For atomic transitions it is convenient to use atomic units $\hbar = m_e = |e| = 1$. In these units, the dependence of electron energies and transition frequencies on α appears due to the relativistic corrections. It is convenient to present frequencies of atomic transitions in a form

$$\omega(x) = \omega_0 + qx, \tag{1}$$

where $x = (\alpha/\alpha_0)^2 - 1$, ω_0 and α_0 are the present values of the transition frequency and the fine-structure constant, and q is the sensitivity coefficient which can be found by varying the value of α in computer codes:

$$q = \frac{\omega(\Delta x) - \omega(-\Delta x)}{2\Delta x}. \tag{2}$$

We use a small value of Δx ($\Delta x = 0.01$) to avoid nonlinear effects, e.g., those which are caused by level crossing [15].

To calculate transition frequencies, we use a range of methods depending on the number of electrons above closed shells. For atoms with one external electron (e.g., Na I) we use the correlation potential method [16]. In this method the calculations start from the relativistic Hartree-Fock (RHF) procedure for the closed-shell core, with one external electron removed. Then, states of external electrons are calculated by solving RHF-like equations which also include core-valence correlations.

$$(\hat{H}_0 + \hat{\Sigma}_1 - \epsilon_v)\psi_v = 0. \tag{3}$$

TABLE I. Energy levels used in the analysis and comparison of the theory with experiment (cm^{-1}).

Z	Atom/ ion	State		Energy	
				Expt. [18]	Theory
11	Na I	$2p^63p$	$^2P^o_{1/2}$	16956.170	16862
		$2p^63p$	$^2P^o_{3/2}$	16973.366	16881
		$2p^65s$	$^2S_{1/2}$	33200.673	33057
20	Ca I	$3p^64s4p$	$^3P^o_1$	15210.063	15544
		$3p^63d4s$	$^3D_1$	20335.360	19568
		$3p^64s5s$	$^3S_1$	31539.495	31816
		$3p^64s5p$	$^3P^o_0$	36547.688	36766
22	Ti I	$3d^3(^2H)4s$	$a\ ^3H_5$	18141.265	21534
		$3d^3(^2H)4s$	$a\ ^3H_6$	18192.570	21369
		$3d^3(^2H)4p$	$x\ ^3H^o_5$	39152.103	41034
		$3d^3(^2H)4p$	$x\ ^3H^o_6$	39198.323	41050
	Ti II	$3d^2(^1D)4s$	$a\ ^2D_{3/2}$	8710.567	10577
		$3d^2(^1G)4s$	$b\ ^2G_{7/2}$	15265.700	17936
		$3d^2(^3F)4p$	$z\ ^4G^o_{5/2}$	29544.454	29005
		$3d^2(^3F)4p$	$z\ ^2G^o_{7/2}$	34543.380	33930
24	Cr I	$3d^44s^2$	$a\ ^5D_2$	7927.441	7114
		$3d^44s^2$	$a\ ^5D_3$	8095.184	7161
		$3d^4(^5D)4s4p(^3P^o)$	$y\ ^5P^o_1$	29420.864	29204
		$3d^4(^5D)4s4p(^3P^o)$	$y\ ^5P^o_2$	29584.571	29284
23	V I	$3d^4(^5D)4s$	$a\ ^6D_{9/2}$	2424.809	2753
		$3d^3(^4F)4s4p(^3P^o)$	$z\ ^6D^o_{9/2}$	18438.044	15575
26	Fe I even	$3d^7(^4F)4s$	$a\ ^3F_2$	12968.554	11964
		$3d^7(^4P)4s$	$a\ ^5P_3$	17550.181	23061
		$3d^7(^4P)4s$	$a\ ^5P_1$	17927.382	22558
		$3d^64s^2$	$a\ ^3P_1$	19552.478	24345
		$3d^64s^2$	$a\ ^3H_4$	19788.251	22233
		$3d^64s^2$	$b\ ^3F_3$	20874.482	25230
		$3d^64s^2$	$b\ ^3F_2$	21038.987	25746
	Fe I odd	$3d^7(^4F)4p$	$y\ ^5D^o_2$	33801.572	33476
		$3d^6(^5D)4s4p(^3P^o)$	$z\ ^3P^o_2$	33946.933	33572
		$3d^7(^4F)4p$	$y\ ^5D^o_0$	34121.603	34050
		$3d^7(^4F)4p$	$z\ ^3G^o_3$	36079.372	35648
		$3d^6(^5D)4s4p(^1P^o)$	$y\ ^5P^o_2$	37157.566	39130
		$3d^7(^4F)4p$	$y\ ^3F^o_3$	37162.746	37388
		$3d^7(^4F)4p$	$y\ ^3D^o_1$	38995.736	39402
28	Ni I	$3d^8(^1D)4s^2$	$^1D_2$	13521.347	15768
		$3d^9(^2D)4p$	$^1P^o_1$	32982.260	30508
		$3d^9(^2D)4p$	$^3D^o_3$	29668.893	28002

Here $\hat{H}_0$ is the RHF Hamiltonian, $\hat{\Sigma}_1$ is a single-electron nonlocal operator (correlation potential) which describes the correlation interaction of an external electron with the core. We calculate $\hat{\Sigma}_1$ in the lowest, second order of the many-body perturbation theory using the B-spline technique [17]. Index v in (3) numerates states of the valence electron. Solutions of (3) are usually called Bruekner orbitals (BOs). Transition frequencies are found as a difference between two BO energies, $\omega_{vw} = \epsilon_v - \epsilon_w$. Calculated energies of the states of Na I which are used in the analysis are compared with experimental data in Table I.

For atoms with two external electrons (e.g., Ca I) we use a combination of the configuration interaction and many-body perturbation theory (CI + MBPT, [19]). Calculations are performed in the V^{N-2} approximation [20]. The self-consistent Hartree-Fock procedure is done for the double ionized ion. Single-electron basis states for valence electrons are calculated in the field of the ion using the B-spline technique similar to how it is done for a single-valence-electron atom. The effective CI Hamiltonian for two valence electrons has the form

$$\hat{H}^{\rm CI} = \hat{h}_1(r_1) + \hat{h}_1(r_2) + \hat{h}_2(r_1, r_2). \tag{4}$$

Here $\hat{h}_1 = \hat{H}_0 + \hat{\Sigma}_1$ is a single-electron part of the Hamiltonian. It includes the RHF operator $\hat{H}_0$ and the correlation potential $\hat{\Sigma}_1$, the same as in (3). The two-electron part of the CI Hamiltonian is the sum of the Coulomb interaction and correlation operator Σ_2, $\hat{h}_2(r_1, r_2) = e^2/|r_1 - r_2| + \hat{\Sigma}_2(r_1, r_2)$. The latter can be understood as screening of the Coulomb interaction between valence electrons by core electrons (see Ref. [19] for details). Calculated energies of the states of Ca I which are used in the analysis are compared with experimental data in Table I.

For atoms with more than two external electrons (Ti I, Ti II, Cr I, V I, Fe I, Ni I) we use a combination of the configuration interaction method with the perturbation theory (the CIPT method [21]). All electrons above the Ar-like core are considered as external electrons and treated with the CI approach. The CI Hamiltonian has a form

$$\hat{H}^{\rm CI} = \sum_i^{N_v} \hat{H}_0(r_i) + \sum_{i<j}^{N_v} e^2/r_{ij}, \tag{5}$$

where $\hat{H}_0$ is the RHF operator, the second term presents the Coulomb interaction between external electrons, and the summation goes over all external (valence) electrons N_v. Correlation operators Σ_1 and Σ_2 are not included for reasons explained below. The number of valence electrons varies from $N_v = 4$ for Ti to $N_v = 10$ for Ni. With the number of external electrons being that large, the number of lines in the CI matrix may go up to $\sim 10^8$ in the standard CI approach. This would make the calculations impossible. Therefore, we use the CIPT [21] approach, in which the off-diagonal matrix elements between high-energy states are neglected. Indeed, it is easy to show that these matrix elements formally appear in a higher order of the perturbation theory and are suppressed by large energy denominators. This allows one to reduce the size of the effective CI matrix by many orders of magnitude. The high-energy states are still included in the correction to the CI matrix elements between low-energy states,

$$\langle a|\hat{H}^{\rm eff}|b\rangle = \langle a|\hat{H}^{\rm CI}|b\rangle + \sum_n \frac{\langle a|\hat{H}^{\rm CI}|n\rangle\langle n|\hat{H}^{\rm CI}|b\rangle}{E - E_n}. \tag{6}$$

Here $\hat{H}^{\rm eff}$ is the effective CI operator, $|a\rangle$ and $|b\rangle$ are many-electron single-determinant low-energy basis states, $|n\rangle$ are high-energy many-electron basis states, E_n is the energy of the high-energy state, $E_n = \langle n|\hat{H}^{\rm CI}|n\rangle$, and E is the energy of the state of interest. Since the latter energy is not known, the CIPT equations, $(H^{\rm eff} - EI)X = 0$, are solved iteratively, using the energy found on the previous iteration to calculate the second term in (6) (see Ref. [21] for details).

Many-electron basis states are constructed using a set of single-electron basis states calculated in the V^{N-1} approximation using the B-spline technique [17]. The V^{N-1} approximation means that the initial RHF procedure is done

TABLE II. Electric dipole transitions used in the analysis and their coefficients of sensitivity to the variation of the fine-structure constant. The energies and notations of the states are taken from the NIST database [18].

Atom/ ion	Lower state		J	Energy (cm^{-1})	Upper state		J	Energy (cm^{-1})	q (cm^{-1})
Na I	$2p^63p$	$^2P^o$	1/2	16956.170	$2p^65s$	^2S	1/2	33200.673	7(1)
Na I	$2p^63p$	$^2P^o$	3/2	16973.366	$2p^65s$	^2S	1/2	33200.673	−11(1)
Ca I	$3p^64s4p$	$^3P^o$	1	15210.063	$3p^64s5s$	^3S	1	31539.495	−69(7)
Ca I	$3p^63d4s$	^3D	1	20335.360	$3p^64s5p$	$^3P^o$	0	36547.688	−475(24)
Ti I	$3d^3(^2H)4s$	$a\,^3H$	5	18141.265	$3d^3(^2H)4p$	$x\,^3H^o$	5	39152.103	440(60)
Ti I	$3d^3(^2H)4s$	$a\,^3H$	6	18192.570	$3d^3(^2H)4p$	$x\,^3H^o$	6	39198.323	460(60)
Ti II	$3d^2(^1D)4s$	$a\,^2D$	3/2	8710.567	$3d^2(^3F)4p$	$z\,^4G^o$	5/2	29544.454	90(90)
Ti II	$3d^2(^1G)4s$	$b\,^2G$	7/2	15265.700	$3d^2(^3F)4p$	$z\,^2G^o$	7/2	34543.380	340(150)
Cr I	$3d^44s^2$	$a\,^5D$	2	7927.441	$3d^4(^5D)4s4p(^3P^o)$	$y\,^5P^o$	1	29420.864	490(60)
Cr I	$3d^44s^2$	$a\,^5D$	3	8095.184	$3d^4(^5D)4s4p(^3P^o)$	$y\,^5P^o$	2	29584.571	490(60)
V I	$3d^4(^5D)4s$	$a\,^6D$	9/2	2424.809	$3d^3(^4F)4s4p(^3P^o)$	$z\,^6D^o$	9/2	18438.044	−600(60)
Fe I	$3d^7(^4F)4s$	$a\,^3F$	2	12968.554	$3d^7(^4F)4p$	$y\,^5D^o$	2	33801.572	−830(400)
Fe I	$3d^64s^2$	$a\,^3P$	1	19552.478	$3d^7(^4F)4p$	$y\,^3D^o$	1	38995.736	2840(300)
Fe I	$3d^7(^4P)4s$	$a\,^5P$	1	17927.382	$3d^6(^5D)4s4p(^1P^o)$	$y\,^5P^o$	2	37157.566	−1500(900)
Fe I	$3d^64s^2$	$a\,^3H$	4	19788.251	$3d^7(^4F)4p$	$z\,^3G^o$	3	36079.372	2710(500)
Fe I	$3d^64s^2$	$b\,^3F$	3	20874.482	$3d^7(^4F)4p$	$y\,^3F^o$	3	37162.746	3010(500)
Fe I	$3d^7(^4P)4s$	$a\,^5P$	3	17550.181	$3d^7(^4P)4p$	$y\,^5D^o$	2	33801.572	340(400)
Fe I	$3d^7(^4P)4s$	$a\,^5P$	1	17927.382	$3d^7(^4F)4p$	$y\,^5D^o$	0	34121.603	430(500)
Fe I	$3d^64s^2$	$b\,^3F$	2	21038.987	$3d^7(^4F)4p$	$y\,^3F^o$	3	37162.746	2870(500)
Fe I	$3d^7(^4P)4s$	$a\,^5P$	1	17927.382	$3d^6(^5D)4s4p(^3P^o)$	$z\,^3P^o$	2	33946.933	−1300(900)
Ni I	$3d^8(^1D)4s^2$	^1D	2	13521.347	$3d^9(^2D)4p$	$^1P^o$	1	32982.260	4950(500)
Ni I	$3d^8(^1D)4s^2$	^1D	2	13521.347	$3d^9(^2D)4p$	^3D	3	29668.893	5500(550)

for a system with one external electron removed. In all considered systems we remove one 4s electron from the ground state and perform the initial RHF calculations for the [Ar]$3d^n4s$ configuration (the [Ar]$3d^3$ configuration for Ti). The basis states above the core are calculated in the field of frozen core. These states are linear combinations of B splines which are the eigenstates of the RHF Hamiltonian with the V^{N-1} potential. In the CIPT method it is important to have good initial approximation so that high states can be treated perturbatively. Therefore, we cannot include correlations between valence electrons and electrons in the Ar-like core via the Σ_1 and Σ_2 operators as is done for a two-electron system, Eq. (4). These operators are well defined only in the V^{N-M} approximation [20], where M is the number of valence electrons. In any other starting potential one has to include subtraction diagrams [19] and even three-body diagrams [22], which is a significant complication to the method. On the other hand, in the considered systems, the correlations are dominated by correlations between valence electrons which are treated pretty accurately in the CI technique. The effect of neglecting the core-valence correlations is smaller than the effect of neglecting the off-diagonal matrix elements between the high-energy states. In all systems considered above we neglect Breit interaction and quantum electrodynamic (QED) corrections. Relativistic corrections are proportional to $Z^2\alpha^2$ and higher powers of $Z\alpha$. Breit and QED corrections have smaller power of Z (less than $Z\alpha^2$ for Breit and $Z^2\alpha^3$ for QED corrections for valence electrons) and numerically are several orders of magnitude smaller. Breit and QED are included in a number of our previous calculations and found to be unimportant at the current level of accuracy for q coefficients. There are exceptions: highly charged ions near level crossing points, where due to the cancellation of different contributions to the small transition energy (deliberately selected) Breit and QED corrections to the values of q have been accurately calculated [23,24]. Ions in the current paper are not of this kind.

Calculated energies of the states of Ti I, Ti II, Cr I, V I, Fe I, and Ni I, which are used in the analysis, are compared with experimental data in Table I. The accuracy is lower than for systems with simple electron structure, like Na I and Ca II. However, it is sufficient for the purposes of the present work. Note that better accuracy may be achieved using fitting parameters. However, empirical fitting parameters may actually depend on α in an uncontrollable way; therefore, we do not use this approach.

The pairs of transitions, which are used in the analysis, are presented in Table II together with the calculated sensitivity coefficients q. Error bars for the q coefficients are estimated by varying computational parameters, such as the value of Δx in Eq. (2), the number of configurations included into the low-energy basis, etc. In most cases the uncertainty is significantly smaller than the value of q. The results show large variation of the values of the sensitivity coefficients q ranging from large negative values to very small values and finally to large positive values. This means that the set of lines is very well suited for the search of the manifestations of the α variation.

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