

The α -dependence of transition frequencies for some ions of Ti, Mn, Na, C, and O, and the search for variation of the fine structure constant.

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We use the relativistic Hartree-Fock method, many-body perturbation theory and configuration-interaction method to calculate the dependence of atomic transition frequencies on the fine structure constant $\alpha = e^2/\hbar c$. The results of these calculations will be used in the search for variation of the fine structure constant in quasar absorption spectra.

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The possibility that the fundamental constants vary is suggested by theories unifying gravity with other interactions (see, e.g. [1, 2, 3] and review [4]). The analysis of quasar absorption spectra by means of the many-multiplet method reveals anomalies which can be interpreted in terms of varying fine structure constant α [5, 6, 7]. The first indication that α might have been smaller at early epoch came from the analysis of magnesium and iron lines [5, 6]. Later inclusion of other lines belonging to many different atoms and ions (Si, Cr, Ni, Zn, etc.) as well as many samples of data from different gas clouds not only confirmed the initial claim, but made it even stronger [7]. However, there are some recent works in which a similar analysis indicates no variation of α in quasar absorption spectra [8, 9]. These works use the same many-multiplet method and the results of our calculations of the relativistic effects in atoms, but analyze different samples of data from a different telescope. It is important to include as much data as possible into the analysis to resolve the differences, and to verify or discard the claim of a varying fine structure constant.

It is natural to analyze fine structure intervals in the search of variation of α . Indeed, initial searches of variation of α in quasar absorption spectra were based on alkali-doublet lines (alkali-doublet method) [10, 11, 12] and on the fine structure of O III [13]. However, all of the present evidence for varying fine structure constant has come from the analysis of the $E1$ -transition frequencies (many-multiplet method) rather than fine structure intervals. These frequencies are about an order of magnitude more sensitive to the variation of α [6]. However, the corresponding analysis is much more complicated. One needs to perform accurate *ab initio* calculations of the atomic structure to reveal the dependence of transition frequencies on the fine structure constant. We have done such calculations for many atoms and ions in our previous works [14, 15]. In the present work we do similar calculations for some other atoms and ions for which data on quasar absorption spectra are available [16], and for which corresponding calculations have not previously

been done.

We use the relativistic Hartree-Fock (RHF) method as a starting point of our calculations. Correlations are included by means of configuration-interaction (CI) method for many valence electron atoms, or by the many-body perturbation theory (MBPT) and Brueckner-orbital method for single valence electron atoms. The dependence of the frequencies on α is revealed by varying α in computer codes.

The results are presented in the form

$$\omega = \omega_0 + qx, \quad (1)$$

where $x = (\alpha^2/\alpha_0^2) - 1$, α_0 is the laboratory value of the fine structure constant, ω and ω_0 are the frequencies of the transition in quasar absorption spectra and in the laboratory, respectively, and q is the relativistic energy shift that comes from the calculations. Comparing the laboratory frequencies, ω_0 , with those measured in the quasar absorption spectra, ω , allows one to obtain the value of α billions of years ago.

The method of calculations is described in detail in our early works [14, 15]. Here we only discuss the details specific for current calculations.

Some atoms and ions considered in the present work represent open-shell (many valence electron) systems. Therefore, the Hartree-Fock procedure needs to be further specified. The natural choice is to remove all open-shell electrons and start the Hartree-Fock calculations for the closed-shell core. However, this usually leads to poor convergence of the subsequent CI method. Better convergence can be achieved using the so called V^{N-1} approximation in which only one valence electron is removed. Since we calculate not only the ground state but also excited states of different configurations, it is convenient to remove the electron which changes its state in the transition. Single-electron basis states for valence electrons are calculated in the V^{N-1} potential of the frozen-core.

The V^{N-1} potential corresponds to an open-shell system. We include the contribution of the open shells into the Hartree-Fock potential as if they were totally filled and then multiply them by a weighting coefficient. Note that this procedure must not destroy the cancellation of the self-action (we would like to remind the reader that there is exact cancellation between direct and exchange

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self-action in the Hartree-Fock equations for the closed-shell systems).

For the CI calculations we use B-splined single-electron basis set similar to those developed by Johnson *et al* [17, 18, 19]. The main difference is that we use the open-shell RHF Hamiltonian described above to calculate the B-splined states.

There are two major sources of inaccuracy in the standard CI calculations. One is incompleteness of the basis set and another is core-valence correlations. We use a fitting procedure to model both effects. We add an extra term into a single-electron part of the Hamiltonian for the valence electrons:

$$U(r) = -\frac{\alpha_c}{2(r^4 + a^4)}. \quad (2)$$

Here α_c is the polarizability of the atomic core and a is a cut-off parameter that is introduced to remove the singularity at $r = 0$. We use $a = a_b$ (Bohr radius) and treat α_c as a fitting parameter. The values of α_c for each partial wave (s, p, d) are chosen to fit the experimental energy levels of the many-electron atom.

The term (2) describes polarization of the atomic core by valence electrons. It can be considered as a semi-empirical approximation to the correlation interaction of a particular valence electron with the core. It also allows us to improve the convergence of the CI calculations by modifying the single-electron basis states. Our calculations for rare-earth ions [20, 21] have demonstrated that using this term allows one to obtain good accuracy of calculations with the minimum number of single-electron basis states (one in each partial wave in the cited works).

Below we present the details and results of calculations for the atoms and ions considered. All transition frequencies are presented with respect to the ground state. Therefore we use the term “energy levels” instead. If a transition between excited states is needed, the corresponding relativistic energy shift q is the difference between the level shifts ($q_{2 \rightarrow 1} = q_2 - q_1$).

a. Manganese ($Z = 25$): The ground state of Mn^+ is $3d^5 4s \ ^7S_3$ and we need to consider transitions into the $3d^4 4s 4p$ configuration. Earlier we also considered transitions to the states of the $3d^5 4p$ configuration [14]. Since in the present work we use different basis set, we have repeated calculations for this configuration in order to check their accuracy.

The RHF calculations are done in the V^{N-1} approximation with the $3d^5$ configuration of external electrons. The $4s, 4p$ and higher states are calculated in the same V^{N-1} potential. We use $\alpha_c = 2.05a_B^3$ for the p -wave as a fitting parameter (see formula (2)). The results are presented in Table I. Fitting changes both energies and q -coefficients by less than 10%, and agreement with previous calculations is also within 10%. Therefore, we use 10% as a conservative estimate of the accuracy of q .

Note that the relativistic shift is positive for the $s - p$ single-electron transitions and negative for the $d - p$ transitions. Having transitions with different signs of q -

TABLE I: Energies and relativistic energy shifts (q) for Mn^+ (cm^{-1})

State	Energy			q	
	theory		experiment	this work	[15]
	no fitting	fitted	[22]		
$3d^5 4p \ ^1P_2$	36091	38424	38366	869	918
$3d^5 4p \ ^7P_3$	36252	38585	38543	1030	1110
$3d^5 4p \ ^7P_4$	36483	38814	38807	1276	1366
$3d^4 4s 4p \ ^7P_2$	97323	83363	83255	-3033	
$3d^4 4s 4p \ ^7P_3$	97554	83559	83376	-2825	
$3d^4 4s 4p \ ^7P_4$	97858	83818	83529	-2556	

TABLE II: Energies and relativistic energy shifts (q) for Ti^+ and Ti^{2+} (cm^{-1})

State		Energy			q
		theory no fitting	fitted	experiment [22]	
Ti ⁺					
$3d^2 4p$	$^4 G_{5/2}$	27870	29759	29544	396
$3d^2 4p$	$^4 F_{3/2}$	28845	30691	30837	541
$3d^2 4p$	$^4 F_{5/2}$	28965	30813	30959	673
$3d^2 4p$	$^4 D_{1/2}$	30582	32416	32532	677
$3d^2 4p$	$^4 D_{3/2}$	30670	32510	32603	791
$3d 4s 4p$	$^4 D_{1/2}$	50651	52185	52330	-1564
Ti ²⁺					
$3d 4p$	$^3 D_1$	80558		77000	-1644

coefficients in the same atom (ion) helps to fight systematic errors in the search for variation of α (see Ref. [14] for details).

b. Titanium ($Z = 22$): We perform calculations for both Ti^+ and Ti^{2+} starting from the same RHF approximation, and using the same single-electron basis set. The ground state of Ti^+ is $3d^2 4s \ ^4F_{3/2}$ and we need to consider transitions into states of the $3d^2 4p$ configuration. The ground state of Ti^{2+} is $3d^2 \ ^3F_2$ and we need to consider transitions into the states of the $3d 4p$ configuration. Therefore it is convenient to do the RHF calculations for the Ti^{2+} ion with the $3d^2$ open-shell configuration. The $4s, 4p$ and other basis states for the CI method are calculated in the frozen-core field of Ti^{2+} .

The fitting parameters chosen are $\alpha_c = 0.38a_B^3$ for s -electrons and $\alpha_c = 0.065a_B^3$ for d -electrons. The results are presented in Table II. As in the case of Mn^+ , there are negative and positive relativistic shifts. The effects of fitting and change of basis set does not exceed 10%. The values of the q -coefficients for titanium are consistent with calculations for other atoms and with semi-empirical estimations using the formulas presented in [14]. In particular, the values of the negative q -coefficients for the $d - p$ transitions are very close to the values for similar transitions in Cr II [14]. The positive coefficients for Ti^+ are very close to those for Mn^+ after rescaling by Z^2 according to the semi-empirical formula [14].

TABLE III: Energies and relativistic energy shifts (q) for Na (cm^{-1})

State		Energy		q
		theory	experiment [22]	
$3p$	$^2P_{1/2}$	16858	16956	45
$3p$	$^2P_{3/2}$	16876	16973	63
$4p$	$^2P_{1/2}$	30124	30267	53
$4p$	$^2P_{3/2}$	30130	30273	59

TABLE IV: Energies and relativistic energy shifts (q) for the carbon atom and its ions (cm^{-1})

State		Energy		q
		theory	experiment [22]	
C				
$2s2p^3$	3D_3	66722	64087	151
$2s2p^3$	3D_1	66712	64090	141
$2s2p^3$	3D_2	66716	64091	145
$2s2p^3$	3P_1	75978	75254	111
$2s2p^3$	3S_1	100170	105799	130
C ⁺				
$2s^22p$	$^2P_{1/2}$	74	63	63
$2s2p^2$	$^2D_{5/2}$	76506	74930	179
$2s2p^2$	$^2D_{3/2}$	76503	74933	176
$2s2p^2$	$^2S_{1/2}$	97993	96494	161
C ²⁺				
$2s2p$	1P_1	104423	102352	162
C ³⁺				
$2p$	$^2P_{1/2}$	65200	64484	104
$2p$	$^2P_{3/2}$	65328	64592	232

c. Sodium ($Z = 11$): In contrast to the ions considered above, sodium is an atom with one external electron above closed shells. Its ground state is $1s^22s^22p^63s^2S_{1/2}$. Very accurate calculations are possible for such systems by including certain types of correlation diagrams to all orders (see, e.g. [23, 24]). However, since both relativistic and correlation effects for sodium are small we use a simplified approach. We calculate the correlation potential $\bar{\Sigma}$ (the average value of this operator is the correlation correction to the energy of the external electron) in the second order only. Then we use it to modify the RHF equations for the valence electron and to calculate the so called Brueckner-orbitals. Note that due to iterations of $\bar{\Sigma}$ certain types of correlation diagrams are still included in all orders in this procedure. The final accuracy of the energy is better than 1%, and for the fine structure accuracy is 2-6% (see Table III). We believe that the accuracy for the relativistic shifts q is on the same level.

d. Carbon ($Z = 6$): Relativistic effects for carbon and its ions are small and calculations can be done without fitting parameters. The ground state of neutral carbon is $1s^22s^22p^2^3P_0$. Our RHF calculations for this

atom include all electrons, however, since we need to consider configurations with excitations from both $2s$ and $2p$ states, we treat both as valence states in CI.

TABLE V: Energies and relativistic energy shifts (q) for oxygen ions (cm^{-1})

State		Energy		q
		theory	experiment [22]	
O ⁺				
$2s2p^4$	$^4P_{5/2}$	122620	119873	346
$2s2p^4$	$^4P_{3/2}$	122763	120000	489
$2s2p^4$	$^4P_{1/2}$	122848	120083	574
O ²⁺				
$2s2p^3$	3D_1	121299	120058	723
$2s2p^3$	3P_1	143483	142382	726
O ³⁺				
$2s2p^2$	$^2D_{3/2}$	129206	126950	840
O ⁵⁺				
$1s^22p$	$^2P_{1/2}$	97313	96375	340
$1s^22p$	$^2P_{3/2}$	97913	96908	872

For neutral carbon we have performed the calculations for the ground state configuration as well as for excited configurations $2s^22p3s$, $2s2p^3$, $2s^22p4s$, $2s^22p3d$, $2s^22p4d$, $2s^22p5d$ and $2s^22p6d$. However, we present in Table IV only results for the $2s2p^3$ configuration. The relativistic energy shift for all other configurations is small ($q < 50 \text{ cm}^{-1}$). This is smaller than uncertainty of the q -coefficients for heavier atoms and ions. Since the analysis of quasar spectra is based on comparison of the relativistic effects in light and heavy atoms (ions), small relativistic energy shifts in light atoms can be neglected. The q -coefficients for the $2s2p^3$ configuration are larger because this configuration corresponds to the $2s - 2p$ transition from the ground state. These are the lowest valence single-electron states with the largest relativistic effects. Other excited configurations correspond to the $2p - ns$ or $2p - nd$ ($n \geq 3$) transitions. However, relativistic energy shifts for higher states are smaller [14].

The calculations for C²⁺ and C³⁺ are done in the potential of the closed-shell (helium) core. As can be seen from Table IV, accuracy for the energies is within 10%. We estimate the accuracy of q -coefficients at around 10-20%.

e. Oxygen ($Z = 8$): Relativistic effects for oxygen ions are comparatively large, and become larger with increasing electric charge. This is in agreement with semi-empirical formulae presented in [14]. For neutral oxygen, however, q -coefficients are approximately 20 cm^{-1} or less; these results are not presented here.

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