Calculation of the dependence of transition frequencies on the fine structure constant and the search for variation of $\alpha$ in QSO spectra

J. C. Berengut, V. A. Dzuba, V. V. Flambaum and M. V. Marchenko

School of Physics, University of New South Wales, Sydney 2052, Australia

(Dated: January 29, 2022)

We calculate the dependence of atomic transition frequencies on the fine structure constant, $\alpha = e^2/\hbar c$, for some ions of Ti, Mn, Na, C, and O. The results of these calculations will be used in the search for variation of $\alpha$ in quasar absorption spectra.

PACS numbers: PACS: 31.30.Jv, 06.20.Jr 95.30.Dr

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 reveals anomalies which can be interpreted in terms of varying fine structure constant $\alpha$ [5, 6, 7]. The first indication that $\alpha$ might have been smaller at early epoch came from the analysis of magnesium and iron lines [5, 6]. However, there are some recent works in which a similar analysis indicates no variation of $\alpha$ in quasar absorption spectra [5]. 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 $\alpha$. Indeed, initial searches of variation of $\alpha$ 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 $\alpha$ [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 $\alpha$ is revealed by varying $\alpha$ in computer codes.

The results are presented in the form

$$\omega = \omega_0 + qx,$$

where $x = (\alpha^2/\alpha_0^2) - 1$, $\alpha_0$ is the laboratory value of the fine structure constant, $\omega$ and $\omega_0$ 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, $\omega_0$, with those measured in the quasar absorption spectra, $\omega$, allows one to obtain the value of $\alpha$ billions of years ago.

The method of calculations is described in detail in our early works [14]. 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 RHF 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 RHF 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 self-action in the RHF equations for the closed-shell systems).

For the CI calculations we use a B-splined single-
electron basis set similar to those developed by Johnson et al. 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 for valence electrons, 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:

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

Here \( \alpha_c \) 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 \( a = a_0 \) (Bohr radius) and treat \( \alpha_c \) as a fitting parameter. The values of \( \alpha_c \) for each partial wave \( (s, p, d) \) are chosen to fit the experimental energy levels of the many-electron atom.

The term 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 sets. Our calculations for rare-earth ions 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 \( 3d^54s^7S \) and we need to consider transitions into the \( 3d^44s4p \) configuration. Earlier we also considered transitions to the states of the \( 3d^54p \) configuration. Since in the present work we use a 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 \( \alpha_c = 2.05a_0^2 \) for the \( p \)-wave as a fitting parameter in Eq. (2). The results are presented in Table 1.

We have done several tests to obtain the error estimates. Fitting changes both energies and \( q \)-coefficients by less than 6% for all transitions, and the agreement with previous calculations is within 15%. We note that the accuracy of the fine structure splitting is significantly worse than this, especially for the upper levels. In some sense this is unsurprising: the fine structure splitting is much smaller than the total relativistic effect due to the strong cancellation between levels. Nonetheless, we may try to fit the splitting using some parameter, and see how \( q \) changes. In fact we have done this by varying \( \alpha \) itself. The splitting for the higher levels becomes very close to experiment at approximately \( x = -0.5 \), and at this point \( q \) is within 1% of the value at \( x = 0 \). This is a similar error estimation procedure as that used in [13] for Ni II, and it shows that \( q \) is insensitive to the fine structure splitting. In another test, we have fit the fine structure splitting by introducing screening parameters before the Coulomb integrals in the CI code. This models the effect of screening of the valence electrons by the core electrons. Again, \( q \) changes by less than 15%.

More worrying is the possibility of level misidentification. This can occur due to misidentification in the tables, or alternatively in the CI results. The Mn\(^+\) spectra contains two \( 3d^44s4p \) \( 7P \) multiplets in close proximity. It is possible (although unlikely) that they are swapped in the computer code. The \( q \) values for the other multiplet are approximately 15% smaller than for the required transitions. Therefore, we use 15% 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 \( q \)-coefficients in the same atom (ion) helps to fight systematic errors in the search for variation of \( \alpha \).

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 \( 3d^24s \) \( 4F_{3/2} \) and we need to consider transitions into states of the \( 3d^24p \) and \( 3d4s4p \) configurations. The ground state of Ti\(^{2+}\) is \( 3d^2 \) \( 3F_3 \) 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 \( \alpha_c = 0.38a_0^2 \) for \( s \)-electrons and \( \alpha_c = 0.065a_0^2 \) for \( d \)-electrons. The results are presented in Table 1. 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 par-

| State | \( \omega_0 \) (cm\(^{-1}\)) | \( q \) (cm\(^{-1}\)) |
|-------|-----------------|-----------------|
| theory | experiment no fitting fitted | this work [14] |
| \( 3d^44p \) \( 7P_1^0 \) | 36536 38424 38366 | 869 (150) 986 |
| \( 3d^44p \) \( 7P_3^0 \) | 36519 38585 38543 | 1030 (150) 1148 |
| \( 3d^44p \) \( 7P_5^0 \) | 36755 38814 38807 | 1276 (150) 1420 |
| \( 3d^44s4p \) \( 7P_1^0 \) | 84092 83363 83256 | -3033 (450) |
| \( 3d^44s4p \) \( 7P_3^0 \) | 84319 83559 83376 | -2825 (450) |
| \( 3d^44s4p \) \( 7P_5^0 \) | 84619 83918 83529 | -2556 (450) |
ticular, the values of the negative q-coefficients for the 
d − p transitions in Cr II [14]. The positive coefficients for 
Ti++ are very close to those for Mn++ after rescaling by 
Z² according to the semi-empirical formula [14]. The 
q-coefficients for the 3d²4p²F₀° states closely match in-
dependent calculations of [22].

TABLE II: Energies and relativistic energy shifts (q) for Ti+
and Ti²⁺.

| State     | ω₀ (cm⁻¹) | q (cm⁻¹) |
|-----------|-----------|----------|
|           | no fitting | fitted    |
| Ti⁺       |           |          |
| 3d²4p     | 4G₁⁰/₂     | 28097    | 29759    | 29544 | 396 (50) |
| 3d²4p     | 4F⁺⁰/₂     | 29401    | 30691    | 30837 | 541 (50) |
| 3d²4p     | 4F⁻⁰/₂     | 20521    | 30813    | 30959 | 673 (50) |
| 3d²4p     | 4D⁺⁰⁰/₂    | 31143    | 32416    | 32532 | 677 (50) |
| 3d²4p     | 4D⁻⁰⁰/₂    | 31227    | 32510    | 32603 | 791 (50) |
| 3d4s4p    | 4D₁⁺⁰    | 50889    | 52185    | 52339 | -1564 (150) |
| 3d4s4p    | 4F₀₁/₂    | 51341    | 52330    | -1783 (300) |
| Ti²⁺      |           | 80558    | 77000    | -1644 (150) |

Figure II shows the dependence of the highly excited 
3d4s4p levels of Ti⁺ on α². The data points are gen-
erated from a highly saturated CI, without any fitting 
parameters. The dependence is very close to linear, 
and hence there is no level pseudo-crossing in the code. 
This does not completely exclude the possibility that the 
4F₀° and 4D₀° levels are strongly mixed (this could be 
checked and accounted for if the experimental g-factors 
were known [17], but they are not available). In the case 
of strong mixing, q lies somewhere between that of the 
two states, thus we have increased the 4F₀° error to in-
clude this possibility.

c. Sodium (Z = 11): In contrast to the ions consid-
erered above, sodium has only one external electron above 
closed shells. Its ground state is 1s²2s²2p⁶3s²3p₁/₂. Very 
accurate calculations are possible for such systems by in-
cluding certain types of correlation diagrams to all orders 
(see, e.g. [24, 25]). However, since both relativistic and 
correlation effects for Na are small we used a simplified 
approach. We calculate the correlation potential Σ (the 
average value of this operator is the correlation corre-
tion to the energy of the external electron) in the second 
order of MBPT, and 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 Σ cer-
tain 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 with-
out fitting parameters. The ground state of neutral car-
bon is 1s²2s²2p² 3P₀. Our RHF calculations for this 
atom include all electrons, however, since we need to con-
sider configurations with excitations from both 2s and 2p 
states, we treat both as valence states in CI.

For neutral carbon we have performed the calculations 
for the ground state configuration as well as for excited 
configurations 2s²2p³s, 2s²2p³, 2s²2p⁴s, 2s²2p³d, 
2s²2p⁴d, 2s³2p⁵d and 2s²2p⁶d. However, we present in 
Table IV only results for the 2s²⁵ configuration. The 
relativistic energy shift for all other configurations is 
small (|q| < 100 cm⁻¹). This is smaller than the un-
certainty in the q-coefficients for heavier ions. Since 
the analysis of quasar spectra is based on comparison of the 
relativistic effects in light and heavy atoms (ions), small
TABLE IV: Energies and relativistic energy shifts ($q$) for the carbon atom and its ions (cm$^{-1}$)

| State   | $\omega_0$ (cm$^{-1}$) | $q$ (cm$^{-1}$) |
|---------|-------------------------|-----------------|
| $2s2p^3$ $^3D_2^0$     | 66722             | 64087           | 151 (60)        |
| $2s2p^3$ $^3D_2^o$      | 66712             | 64090           | 141 (60)        |
| $2s2p^3$ $^3D_2^+$      | 66716             | 64091           | 145 (60)        |
| $2s2p^3$ $^3P_2^0$      | 75978             | 75254           | 111 (60)        |
| $2s2p^3$ $^3S_1^o$      | 100170            | 107599          | 130 (60)        |

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 C$^{2+}$ and C$^{3+}$ 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%.

TABLE V: Energies and relativistic energy shifts ($q$) for oxygen ions

| State   | $\omega_0$ (cm$^{-1}$) | $q$ (cm$^{-1}$) |
|---------|-------------------------|-----------------|
| $2s2p^4$ $^4P_{3/2}$   | 122620             | 119873          | 346 (50)        |
| $2s2p^4$ $^4P_{3/2}$   | 122763             | 120000          | 489 (50)        |
| $2s2p^4$ $^4P_{1/2}$   | 122848             | 120873          | 574 (50)        |
| $2s2p^3$ $^3D_2^+$     | 121299             | 120058          | 723 (50)        |
| $2s2p^3$ $^3P_1^+$     | 143483             | 142382          | 726 (50)        |
| $2s2p^2$ $^2D_{5/2}$   | 129206             | 126950          | 840 (50)        |
| $1s^22p^2$ $^2P_{5/2}^o$ | 96501         | 96375           | 309 (50)        |
| $1s^22p^2$ $^2P_{5/2}^2$ | 97091         | 96908           | 913 (50)        |

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 transitions in neutral oxygen, however, $|q| < 20$ cm$^{-1}$; these results are not presented here.

This work was supported by the Australian Research Council.

[1] W. J. Marciano, Phys. Rev. Lett. 52, 489 (1984).
[2] J. D. Barrow, Phys. Rev. D 35, 1805 (1987).
[3] T. Damour and A. M. Polyakov, Nucl. Phys. B 423, 596 (1994).
[4] J.-P. Uzan, Rev. Mod. Phys. 75, 403 (2003).
[5] J. K. Webb, V. V. Flambaum, C. W. Churchill, M. J. Drinkwater, and J. D. Barrow, Phys. Rev. Lett. 82, 884 (1999).
[6] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. Lett. 82, 888 (1999).
[7] J. K. Webb, M. T. Murphy, V. V. Flambaum, V. A. Dzuba, J. D. Barrow, C. W. Churchill, J. X. Prochaska, and A. M. Wolfe, Phys. Rev. Lett. 87, 091301 (2001).
[8] R. Quast, D. Reimers, and S. A. Levshakov, astro-ph/0311280.
[9] R. Srianand, H. Chaud, P. Petitjean, and B. Aracil, astro-ph/0401094, astro-ph/0402177.
[10] A. M. Wolfe, R. L. Brown, and M. S. Roberts, Phys. Rev. Lett. 37, 179 (1976).
[11] L. L. Cowie and A. Songaila, Astrophys. J. 453, 596 (1995).
[12] D. A. Varshalovich, V. E. Panchuk, and A. V. Ivanchik, Astron. Lett. 22, 6 (1996).
[13] J. N. Bahcall, C. L. Steinhardt, and D. Schlegel, Astrophys. J. 600, 520 (2004).
[14] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. A 59, 230 (1999).
[15] V. A. Dzuba, V. V. Flambaum, M. G. Kozlov, and M. V. Marchenko, Phys. Rev. A 66, 022501 (2002).
[16] M. T. Murphy, private communication (2003).
[17] W. R. Johnson and J. Sapirstein, Phys. Rev. Lett. 57, 1126 (1986).
[18] W. R. Johnson, M. Idrees, and J. Sapirstein, Phys. Rev. A 35, 3218 (1987).
[19] W. R. Johnson, S. A. Blundell, and J. Sapirstein, Phys. Rev. A 37, 307 (1988).
[20] V. A. Dzuba, O. P. Sushkov, W. R. Johnson, and U. I. Safonova, Phys. Rev. A 66, 032105 (2002).
[21] V. A. Dzuba, U. I. Safonova, and W. R. Johnson, Phys. Rev. A 68, 032503 (2003).
[22] C. E. Moore, Atomic Energy Levels - v. II, NSRDS-NBS 35 (U. S. Government Printing Office, Washington DC, 1971).
[23] M. G. Kozlov, private communication (2004).
[24] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, Phys. Lett. A 140, 493 (1989).
[25] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. A 43, 3407 (1991).