

Space-Time Variation of Physical Constants and Relativistic Corrections in Atoms

V. A. Dzuba,* V. V. Flambaum, and J. K. Webb

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

(Received 12 February 1998)

High-redshift absorption systems detected in the optical spectra of quasars provide a powerful tool for constraining possible spatial and temporal variations of physical “constants” in the Universe. It is demonstrated that high sensitivity to the variation of the fine structure constant α can be obtained from a comparison of the spectra of heavy and light atoms. We have performed calculations for Mg I, Mg II, Cr II, and Fe II for which accurate quasar and laboratory spectra are available. Some possibilities for observing enhanced effects in variations of the fundamental constants in laboratory measurements are also discussed. [S0031-9007(98)08271-4]

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

A possible variation of the fundamental physical constants in the expanding Universe was first suggested by Dirac [1]. The subject is of particular current interest because of the new possibilities opened up by the structure of unified theories, such as string theory and M theory, which lead us to expect that additional compact dimensions of space may exist. The “constants” seen in the three-dimensional subspace of the theory will vary at the same rate as any change occurring in the scale lengths of these extra compact dimensions (see, e.g., [2]). Quasar absorption systems present ideal laboratories in which to search for any temporal or spatial variation of fundamental constants by comparing atomic spectra from the distant objects with laboratory spectra (see, e.g., [3], and references therein).

The energy scale of atomic spectra, in the nonrelativistic limit, is given by the atomic unit $\frac{me^4}{\hbar^2}$. In this limit, all atomic spectra are proportional to this quantity and no change of the fundamental constants can be detected. Indeed, any change in the atomic unit will be absorbed in the determination of the redshift parameter $1 + z = \frac{\omega}{\omega'}$ (ω' is the redshifted frequency of the atomic transition, and ω is this frequency in the laboratory). However, any change in the fundamental constants can be found by measuring the relative size of relativistic corrections, which are proportional to α^2 , where $\alpha = e^2/\hbar c$ is the fine structure constant [4].

It would seem natural to constrain any change from measurements of the spin-orbit splitting within a fine structure multiplet. However, this is not the most efficient method, and it may even give incorrect results, since other relativistic effects are ignored. The aim of this Letter is to demonstrate that a change in α produces an order of magnitude larger effect in the difference between transition frequencies in heavy and light atoms (or molecules) compared to the difference for transitions within a single multiplet.

We have calculated the dependence of the transition frequencies on α for Fe II, Cr II, Mg I [see Eq. (3)], and Mg II [see Eq. (2)] where accurate data exist for

both laboratory and quasar spectra. Other possibilities include comparisons of different optical transitions, for example, s - p and p - d , in the same atom or molecule, or comparisons of microwave transitions in molecules which contain rotational and hyperfine intervals.

We also propose two other potential methods (probably more suited to laboratory experiments than to high redshift observations) to detect any possible changes in α . The first is to use transitions between “accidentally” degenerate levels in the same atom or molecule. This degeneracy would be highly sensitive to very small changes in α . For example, in the Dy atom there are two degenerate opposite-parity levels [5]. The frequency of the $E1$ transition between them is smaller than the hyperfine splitting of each level. As a result, the relative effect of a change in α is enhanced by 5 orders of magnitude (the ratio of the size of the relativistic effect to the transition frequency). Similar experiments with accidentally degenerate molecular levels belonging to different electron terms are also sensitive to very small changes in the ratio of the nucleon to electron masses. This is because the difference in electron energies may be compensated by the difference in the vibrational and rotational energies of the nuclei. As is known, the nuclear mass is a function of the strong interaction constants and vacuum condensates. The problem here is to find narrow width “degenerate” levels.

The second potential method is to make accurate measurements of the difference between the frequencies of two narrow width transitions in different atoms or molecules. If this difference is very small it can be measured with a very high absolute accuracy since limitations associated with the precision of the absolute frequency calibration would be irrelevant (see, e.g., measurements in Hg II and H [6,7]). For the Hg II $35\,514\text{ cm}^{-1}$ line the frequency shift corresponding to $\Delta\alpha/\alpha = 10^{-15}$ is about 3 Hz which is bigger than the natural linewidth of 1.8 Hz.

To explain the advantages of our proposals let us start from simple analytical estimates of the relativistic effects in transition frequencies. The contribution of the relativistic correction to the energy can be obtained as an

expectation value $\langle V \rangle$ of the relativistic perturbation V , which is large in the vicinity of the nucleus only. The wave function of an external electron near the nucleus is presented, e.g., in [8]. A simple calculation of the relativistic correction to the energy of the external electron gives the following result:

$$\begin{aligned} \Delta_n &= -\frac{me^4 Z_a^2}{2\hbar^2} \frac{(Z\alpha)^2}{\nu^3} \left[\frac{1}{j+1/2} - C(j,l) \right] \\ &= \frac{E_n(Z\alpha)^2}{\nu} \left[\frac{1}{j+1/2} - C(j,l) \right], \end{aligned} \quad (1)$$

where Z is the nuclear charge, l and j are the orbital and total electron angular momenta, Z_a is the charge "seen" by the external electron outside the atom, i.e., $Z_a = 1$ for neutral atoms, $Z_a = 2$ for singly charged ions, etc., and ν is the effective principal quantum number, defined by $E_n = -\frac{me^4 Z_a^2}{2\hbar^2 \nu^2}$, where E_n is the energy of the electron. For hydrogenlike ions $\nu = n$, $Z_a = Z$, where n is the principal quantum number. To describe the contribution of many-body effects to the relativistic correction Δ_n we introduced the parameter $C(j,l)$. Indeed, the single-particle relativistic correction increases the attraction of an electron to the nucleus and makes the radius of the electron cloud smaller. As a result, the atomic potential, which is the nuclear potential screened by the core electrons, becomes weaker. This decreases the binding energy of the external electron. Therefore, the many-body effect has the opposite sign to that of the direct single-particle relativistic effect. Accurate many-body calculations described below show $C(j,l)$ for s and p orbitals to be about 0.6. We see that the relativistic correction is large and negative for the lowest $s_{1/2}$ and $p_{1/2}$ states, where ν is small and $j = 1/2$. The fine structure splitting is given by $\Delta_{fs} = E(p_{3/2}) - E(p_{1/2})$. The relativistic correction may be large and positive for the lowest d -states. Equation (1) may be used for the approximate semiempirical estimates of the relativistic corrections.

In spectra of quasar absorption systems, transitions from the ground state have been observed. Understanding how the observed frequencies of these transitions depend on relativistic effects enables us to search for any relative changes in α over the large time span between the early epochs probed by the quasar data and today. The fine splitting in excited states is smaller than the relativistic correction in the ground state, since the density of the excited electron near the nucleus is smaller. Thus the fine splitting of the $E1$ transition from the ground state (e.g., s - p) is substantially smaller than the absolute shift of the frequency of the s - p transition. At $C(j,l) = 0.6$ the relativistic shift of the mean energy of the p electron, $E(p) = 2/3E(p_{3/2}) + 1/3E(p_{1/2})$, is close to zero. Therefore, the average relativistic shift of the s - p transition frequency is mostly given by the energy shift of the s state: $\Delta(p-s) \approx -\Delta(s)$.

The relative size of the relativistic corrections is proportional to Z^2 , so they are smaller in light atoms. Therefore, we can constrain any change in α by comparing transition frequencies in heavy and light atoms (or two heavy atoms like Fe II and Cr II where the relativistic frequency shifts have opposite signs). We stress that the most accurate and effective procedure must include all relativistic corrections and the analysis of all available lines (rather than the fine splitting within one multiplet only).

To obtain accurate values of the relativistic frequency shifts we performed calculations of atomic spectra using many-body perturbation theory. Mg II is a simple system with one external electron above closed shells. In this case we used the complete set of relativistic Hartree-Fock energies and wave functions as a zero approximation and then calculated all second-order correlation corrections in the residual electron-electron interaction (this technique is described in [9]). This *ab initio* calculation reproduces the experimental energy levels of the external electron in Mg II with 0.2% accuracy (the single-electron energy levels in the many-body problem are defined as the ionization energies with a minus sign). To find the value of relativistic corrections we performed calculations for three values of α : $\alpha = \alpha_l$, $\alpha = \sqrt{7/8} \alpha_l$, and $\alpha = \sqrt{3/4} \alpha_l$, where α_l is the laboratory value of α . The calculated relativistic corrections to the energy levels of the external electron are $\Delta(3s) = -189.4$, $\Delta(3p_{1/2}) = -72.1$, $\Delta(3p_{3/2}) = 24.4$, and $\Delta_{fs} = 96.5 \text{ cm}^{-1}$. Note that the many-body corrections change the sign of $\Delta(3p_{3/2})$. A convenient presentation of the final results is given in the following form:

$$\begin{aligned} 3s_{1/2} - 3p_{1/2}: \\ \omega_1 &= 35\,669.298(2) + 119.6\left[\left(\frac{\alpha}{\alpha_l}\right)^2 - 1\right] \text{ cm}^{-1}, \\ 3s_{1/2} - 3p_{3/2}: \\ \omega_2 &= 35\,760.848(2) + 211.2\left[\left(\frac{\alpha}{\alpha_l}\right)^2 - 1\right] \text{ cm}^{-1}. \end{aligned} \quad (2)$$

The first term in each formula is the laboratory value of the frequency (these are averaged over the Mg isotopes; detailed information including isotope shifts can be found in [10,11]), and the second term gives the dependence on α . We changed slightly the values of the calculated coefficients so as to exactly reproduce the experimental value of the fine splitting $\Delta_{fs} = 91.6 \text{ cm}^{-1}$ (at $\alpha = 0$ the fine splitting must vanish).

Now consider atoms with several valence electrons, like Mg I or Fe II. Here we also have s - p transitions from the ground states, and the semiempirical formula (1) can be used to estimate the relativistic frequency shift. However, to accurately calculate the relativistic shift for each transition we performed relativistic many-body calculations for energy levels. We used a relativistic Hartree-Fock method to construct a basis set of one-electron orbitals and a configuration interaction method to obtain the many-electron wave function of valence electrons. Correlations between core and valence electrons were also

included by means of many-body perturbation theory [12]. The details of these calculations will be presented in a longer paper. We obtained the following results for the frequencies of the strong $E1$ transitions from the ground state of Mg I ($3s^2\ ^1S_0 - 3s3p\ ^1P_1$), Fe II ($3d^64s^6D_{9/2}$ to the members of the multiplets $3d^64p\ ^6D$, 6F , and 6P) and Cr II ($3d^5\ ^6S_{5/2}$ to the multiplets $3d^44p\ ^6F$ and 6P), as the functions of α (in cm^{-1}):

$$\begin{aligned}
 \text{Mg I } ^1S_0: & \quad \omega = 35\,051.277(1) + 106x - 10y, \\
 \text{Fe II } ^6D_{9/2}: & \quad \omega = 38\,458.9871(30) + 1394x + 38y, \\
 & \quad ^6D_{7/2}: \quad \omega = 38\,660.0494(30) + 1632x + 0y, \\
 & \quad ^6F_{11/2}: \quad \omega = 41\,968.0642(30) + 1622x + 3y, \\
 & \quad ^6F_{9/2}: \quad \omega = 42\,114.8329(30) + 1772x + 0y, \\
 & \quad ^6F_{7/2}: \quad \omega = 42\,237.0500(30) + 1894x + 0y, \\
 & \quad ^6P_{7/2}: \quad \omega = 42\,658.2404(30) + 1398x - 13y, \\
 \text{Cr II } ^6F_{3/2}: & \quad \omega = 46\,905.17 - 1624x - 25y, \\
 & \quad ^6F_{5/2}: \quad \omega = 47\,040.35 - 1493x - 21y, \\
 & \quad ^6F_{7/2}: \quad \omega = 47\,227.24 - 1309x - 18y, \\
 & \quad ^6P_{3/2}: \quad \omega = 48\,398.941 - 1267x - 9y, \\
 & \quad ^6P_{5/2}: \quad \omega = 48\,491.105 - 1168x - 16y, \\
 & \quad ^6P_{7/2}: \quad \omega = 48\,632.125 - 1030x - 13y, \quad (3)
 \end{aligned}$$

where $x = (\frac{\alpha}{\alpha_l})^2 - 1$, $y = (\frac{\alpha}{\alpha_l})^4 - 1$. The values of the laboratory frequencies ($\alpha = \alpha_l$) were taken from [11,13]. The results for other atoms suitable for the astrophysical measurements (Mn II, Fe I, Ni I, Zn II, Ge II, C II, C IV, N V, O I, Al III, Si II, Si IV, Ca I, Ca II) will be presented elsewhere.

One can use Eqs. (2) and (3) to fit Fe II, Cr II, Mg I, and Mg II lines in quasar absorption systems to constrain any variations in α . We see that the difference between the frequencies for light and heavy atoms have a relativistic effect which is an order of magnitude larger than the difference between frequencies within one multiplet (note that the selection rule $|J_f - J_i| \leq 1$ allows transitions to a few nearby components of each multiplet only). For the species above, the maximal effect is obtained by comparing Fe II and Cr II lines, where the relativistic shifts have opposite signs (since there are $s-p$ transitions in Fe II and $d-p$ transitions in Cr II). Our results for Mg II and Fe II have already been used for the search of the variation of α in Ref. [14].

Equation (1) shows that one should expect the biggest relativistic shift for the $s-d$ (or $d-s$) transitions in heavy atoms. However, these transitions cannot be observed in quasar absorption systems but may be suitable for use in laboratory experiments. The natural linewidth for these $E2$ transitions is very small. Furthermore, very precise frequency measurements of many such transitions already exist since they are used as atomic optical frequency

standards. Among them, the narrow Hg-II transition $5d^{10}6s\ ^2S_{1/2} - 5d^26s^2\ ^2D_{5/2}$ has the biggest relativistic frequency shift: $\omega = 35\,514 - 29\,708x - 9767y\ \text{cm}^{-1}$. Since this is a $d-s$ transition, it has a very large relativistic shift of opposite sign to the $s-p$ transitions above.

One more interesting possibility is to use transitions between accidentally degenerate levels in the same atom. Such metastable levels exist, for example, in the Dy atom: two $J = 10$ opposite parity levels $4f^{10}5d6s$ and $4f^95d^26s$ lying $19\,797.96\ \text{cm}^{-1}$ above the ground state. (This pair of levels was used to study parity nonconservation in Ref. [5].) There are other examples of accidentally degenerate levels in the rare-earth and actinide atoms and many close levels in other heavy atoms and ions (in the absence of degeneracy one should look for $s-d$ or $s-p$ transitions where the relativistic effects are larger). Where ‘‘accidental’’ degeneracy occurs, the contributions of the relativistic corrections to the frequency of the $E1$ transition in a heavy atom ($\sim 1000\ \text{cm}^{-1}$) is compensated by the difference in the Coulomb interaction energies of the two configurations. However, if α varies with time, this compensation will eventually disappear. Thus, we have a correction $\sim 1000\ \text{cm}^{-1}[(\frac{\alpha}{\alpha_l})^2 - 1]$ to the very small ($< 0.01\ \text{cm}^{-1}$) frequency of the transition. One can measure, for example, the time dependence of the ratio of frequencies for transitions between the hyperfine components of these two states. For accidentally degenerate levels belonging to different electron terms in a molecule, one can have enhanced effects of the change of both α and the nucleon mass. In the latter case the enhancement factor is the ratio of the vibration energy to the small frequency of the transition.

We are grateful to O. Sushkov, D. Budker, and J. Vigue for useful discussions.

*Email address: V.Dzuba@unsw.edu.au;

<http://www.phys.phys.unsw.edu.au/~dzuba>

- [1] P. A. M. Dirac, Nature (London) **139**, 323 (1937).
- [2] W. Marciano, Phys. Rev. Lett. **52**, 489 (1984); J. D. Barrow, Phys. Rev. D **35**, 1805 (1987); T. Damour and A. M. Polyakov, Nucl. Phys. **B423**, 596 (1994).
- [3] D. A. Varshalovich and A. Y. Potekhin, Space Sci. Rev. **74**, 259 (1995).
- [4] Other possibilities include comparison of the hyperfine transition frequency with the molecular rotational interval, which at present gives the best limit on the change of $\alpha^2 g_p$ where g_p is the proton magnetic g -factor—see M. J. Drinkwater, J. K. Webb, J. D. Barrow, and V. V. Flambaum, Mon. Not. R. Astron. Soc. **295**, 457 (1998). The best limit on $\alpha^2 g_p m_e/m_p$ was obtained in L. L. Cowie and A. Songaila, Astrophys. J. **453**, 596 (1985), from comparison of the hyperfine and optical lines.
- [5] V. A. Dzuba, V. V. Flambaum, and I. B. Khriplovich, Z. Phys. D **1**, 243 (1986); A. T. Nguyen, D. Budker, D. DeMille, and M. Zolotarev, Phys. Rev. A **56**, 3453 (1997).

- [6] J. C. Bergquist, W. M. Itano, F. Elsner, M. G. Raizen, and D. J. Wineland, *Light Induced Kinetic Effects on Atoms, Ions And Molecules*, edited by L. Mot, S. Gozzini, C. Gabbanini, E. Arimondo, and F. Strumia (ETS Editrice, Pisa, 1991).
- [7] T. Udem, A. Huber, B. Gross, J. Reichert, M. Prevedilli, M. Weitz, and T. Hänsch, Phys. Rev. Lett. **79**, 2646 (1997).
- [8] I. I. Sobelman, *Introduction to the Theory of Atomic Spectra* (Nauka, Moscow, 1977) (in Russian).
- [9] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, J. Phys. B **16**, 715 (1983); V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B **20**, 1399 (1987); V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, Phys. Lett. A **140**, 493 (1989).
- [10] R. E. Drullinger, D. J. Wineland, and J. C. Bergquist, Appl. Phys. **22**, 365 (1980).
- [11] J. C. Pickering, A. P. Thorne, and J. K. Webb, Mon. Not. R. Astron. Soc. (to be published).
- [12] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).
- [13] G. Nave, R. C. M. Learner, A. P. Thorne, and C. J. Harris, J. Opt. Soc. Am. B **8**, 2028 (1991); J. Sugar and C. Corliss, J. Phys. Chem. Ref. Data **14**, Suppl. No. 2 (1985); D. C. Morton, Astrophys. J. Suppl. **77**, 119 (1991); **81**, 883 (1992).
- [14] J. K. Webb, V. V. Flambaum, C. W. Churchill, M. J. Drinkwater, and J. D. Barrow, preceding Letter, Phys. Rev. Lett. **82**, 884 (1999).