# Calculations of the relativistic effects in many-electron atoms and space-time variation of fundamental constants

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Theories unifying gravity and other interactions suggest the possibility of spatial and temporal variation of physical ''constants'' in the Universe. Detection of high-redshift absorption systems intersecting the sight lines towards distant quasars provides a powerful tool for measuring these variations. We have previously demonstrated that high sensitivity to the variation of the fine-structure constant $\alpha$ can be obtained by comparing spectra of heavy and light atoms (or molecules). Here we describe new calculations for a range of atoms and ions, most of which are commonly detected in quasar spectra: Fe II, Mg II, Mg I, C II, C IV, N V, O I, Al III, Si II, Si IV, Ca I, Ca II, Cr II, Mn II, Zn II, Ge II (see the results in Table III). The combination of Fe II and Mg II, for which accurate laboratory frequencies exist, has already been used to constrain $\alpha$ variations. To use other atoms and ions, accurate laboratory values of frequencies of the strong $E1$ transitions from the ground states are required. We wish to draw the attention of atomic experimentalists to this important problem. We also discuss a mechanism which can lead to a greatly enhanced sensitivity for placing constraints on variation on fundamental constants. Calculations have been performed for Hg II, Yb II, Ca I, and Sr II where there are optical transitions with the very small natural widths, and for hyperfine transition in Cs I and Hg II.
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## I. INTRODUCTION

Possible variations of the fundamental physical constants in the expanding Universe are currently of particular interest because of the implications from unified theories, such as string theory and $M$ theory, that additional compact dimensions of space may exist. The ''constants'' seen in our three-dimensional subspace of the theory will vary at the same rate as any change occurring in the scale lengths of the extra compact dimensions (see, e.g., [1–3]). Gas clouds which intersect the sight lines towards distant quasars produce absorption lines. These absorption systems present ideal laboratories in which to search for any temporal or spatial variation of fundamental constants by comparing the observed atomic spectra from the distant objects with laboratory spectra (see, e.g., [4], and references therein).

The energy scale of atomic spectra is given by the atomic unit $me^4/\hbar^2$. In the nonrelativistic limit, all atomic spectra are proportional to this constant and analyses of quasar spectra cannot detect any change of the fundamental constants. Indeed, any change in the atomic unit will be absorbed in the determination of the redshift parameter $z$ ($1+z=\omega/\omega'$, $\omega'$ is the redshifted frequency of the atomic transition, and $\omega$ is the laboratory value). However, any change of the fundamental constants can be found by measuring the relative size of relativistic corrections, which are proportional to $\alpha^2$, where $\alpha=e^2/\hbar c$ is the fine-structure constant [5].

It is natural to search for any changes in $\alpha$ using measurements of the spin-orbit splitting within a specific fine-structure multiplet, and indeed this method has been applied

to quasar spectra by several groups. However, while this method is appealing through its simplicity, it is possible to improve on its efficiency. Also, it may even give incorrect results, since corrections of higher order than $\alpha^2$ are ignored. An order of magnitude sensitivity gain can be achieved by comparing transition frequencies of heavy and light atoms (or molecules) [6,7]. In this paper we extend that previous work, presenting the results of calculations of the dependence of the transition frequencies on $\alpha$ for many atoms and ions where data exist for quasar spectra (see Table III).

Other possibilities for measuring changes in $\alpha$ include comparisons of different optical transitions, such as $s$-$p$ and $p$-$d$, in the same atom or molecule, or comparisons of microwave transitions in molecules which contain rotational and hyperfine intervals. We have also calculated the dependence on $\alpha$ of some atomic microwave and optical frequency standards which could be used for laboratory searches for $\alpha$ variations. For example, one can compare the Hg II $E2$ transition $\omega=35\,514$ cm$^{-1}$ with any narrow line of another atomic or molecular transition having approximately the same frequency. Small frequency differences (which do not require very precise *absolute* calibration) can be measured very accurately. The mercury frequency has a very large relativistic shift which also has a negative sign (usually the shift is positive). Therefore this frequency difference has a very strong $\alpha$ dependence.

Finally, there is an interesting possibility for studying transitions between ''accidentally'' degenerate levels in the same atom or molecule. There are several practically degenerate levels of different electron configurations in rare-earth and actinide atoms. Of course, there are many more possibilities in molecules where there are vibrational and rotational structures. The relativistic corrections to the different energy levels are different and can exceed the very small frequency corresponding to the transition between ''degenerate'' states by many orders of magnitude, i.e., a tiny varia-

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tion of $\alpha$ can change the frequency significantly. Also, there is an interesting dependence on the nucleon mass if the rotational, vibrational, and hyperfine structures are involved. In this case one can measure time dependence of the nucleon mass which is a function of the strong interaction constant. The main problem here is to find a narrow-width transition.

Note that we present all results in this paper assuming that the atomic unit of energy $me^4/\hbar^2$ is constant.

## II. THEORY

### A. Semiempirical estimations

Let us start our calculations using simple analytical estimates of the relativistic effects in transition frequencies. First consider the relativistic corrections to the frequency of an atomic transition in a hydrogenlike atom. The relativistic correction to the energy level is given by (see, e.g., [8])

$$\Delta_n = -\frac{me^4 Z^2}{2\hbar^2} \frac{(Z\alpha)^2}{n^3} \left( \frac{1}{j+1/2} - \frac{3}{4n} \right), \qquad (1)$$

where $Z$ is the nuclear charge, $n$ is the principal quantum number, and $j$ is the total electron angular momentum. This value of the relativistic correction can be obtained as an expectation value $\langle V \rangle$ of the relativistic perturbation $V$, which is only large in the vicinity of the nucleus. Therefore the relativistic correction $\Delta$ is proportional to the electron density near the nucleus $|\Psi(r<a/Z)|^2 \propto Z^3/n^3 a^3$ ($a$ is the Bohr radius, $a/Z$ is the size of the hydrogenlike ion). For an external electron in a many-electron atom or ion the electron density near the nucleus is given by the formula (see, e.g., [9]) obtained in the semiclassical approximation ($n \gg 1$)

$$\left| \Psi\left( r < \frac{a}{Z} \right) \right|^2 \propto \frac{Z_a^2 Z}{\nu^3 a^3}, \qquad (2)$$

where $Z_a$ 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.; $\nu$ is the effective principal quantum number, defined by $E_n = -(me^4/2\hbar^2)/(Z_a^2/\nu^2)$, where $E_n$ is the energy of the electron. For hydrogenlike ions $\nu = n, Z_a = Z$. Thus, to find the single-particle relativistic correction, we should multiply $\Delta$ in Eq. (1) by the ratio of $|\Psi(r<a/Z)|^2$ in the multielectron ion and hydrogenlike ion. The result is

$$\Delta_n = -\frac{me^4 Z_a^2}{2\hbar^2} \frac{(Z\alpha)^2}{\nu^3} \left[ \frac{1}{j+1/2} - \frac{Z_a}{Z\nu} \left( 1 - \frac{Z_a}{4Z} \right) \right]$$

$$\simeq E_n \frac{(Z\alpha)^2}{\nu(j+1/2)}. \qquad (3)$$

The second term in the square brackets is presented to provide a continuous transition from the hydrogenlike ion Eq. (1) to the multielectron ion Eq. (3). In multielectron ions ($Z \gg Z_a$) this term is, in fact, a rough estimate based on the direct calculation of $\langle V \rangle$. We should neglect this small term since there are more important many-body corrections.

We see that the relativistic correction is largest for the $s_{1/2}$ and $p_{1/2}$ states, where $j = 1/2$. The fine-structure splitting is given by

$$\Delta_{ls} = E(p_{3/2}) - E(p_{1/2}) \simeq -\Delta(p_{1/2})/2 \simeq -\Delta(p_{3/2}). \qquad (4)$$

In quasar absorption spectra, transitions from the ground state have been observed. Therefore it is important to understand how the frequencies of these transitions are affected by relativistic effects. 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. As a result, 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. The mean energy of the $p$ electron is defined as

$$E(p) = \frac{2}{3} E(p_{3/2}) + \frac{1}{3} E(p_{1/2}) \simeq E_n(p) - \frac{4}{3} \Delta_{ls}, \qquad (5)$$

where $E_n$ is the nonrelativistic energy. Therefore the relativistic shift of the mean $s$-$p$ transition frequency is given by

$$\Delta(p-s) \simeq -\frac{4}{3} \Delta_{ls} - \Delta(s_{1/2}). \qquad (6)$$

The formulas (3)–(6) do not take into account many-body effects. For example, relativistic corrections change the self-consistent atomic potential. The many-body calculations discussed below show that the relativistic energy shift in atoms with one external electron can be approximately described by the equation

$$\Delta_n = \frac{E_n}{\nu} (Z\alpha)^2 \left[ \frac{1}{j+1/2} - C(Z,j,l) \right], \qquad (7)$$

where $C(Z,j,l)$ is different for different atoms and partial waves but does not depend on the principal quantum number. In many cases $C(Z,j,l) \simeq 0.6$, although noticeable deviations from this value are possible.

It is easy to explain the sign of the many-body effect. The relativistic single-particle correction increases the attraction of an electron to the nucleus and makes the radius of the electron cloud smaller. As a result, the direct Hartree-Fock potential, which is the nuclear potential screened by core electrons, becomes smaller at short distances. This decreases the binding energy of a valence electron. Therefore many-body effects have an opposite sign to the direct effect.

It is also easy to see why $C(Z,j,l)$ does not depend on the energy of the valence electron. The effect of a potential change on short distances on the binding energy of an external electron is proportional to the density of this electron in the vicinity of the nucleus which in turn is proportional to $1/\nu^3$ [see Eq. (2)]. On the other hand, the direct relativistic effect is also proportional to $1/\nu^3$ for the same reason (see Eqs. (2) and (3)]. Therefore the ratio of two effects which is $C(Z,j,l)/(2j+1)$ is practically independent of the energy of the external electron.

The accurate value of the relativistic shift can only be obtained from many-body calculations. However, one can assume that $C(Z,j,l) = 0.6$ and use Eq. (7) for rough estimates of relativistic corrections. This usually gives better

results than a single-particle estimate in Eq. (3). For example, many-body calculations show that, as a rule, the relativistic correction to the energy is negative for $s_{1/2}$ and $p_{1/2}$ states and positive for other states. This behavior is reproduced by Eq. (7) but not by Eq. (3). Apart from that, formula (3) suggests that the correction is largest for $s_{1/2}$ and $p_{1/2}$ states and rapidly decreases with $j$ while many-body calculations show that the correction for $d$ states is sometimes bigger than for $p$ states. This is again reproduced by Eq. (7) where there is a strong cancellation between two terms in the case of $p$ states. Note that this complex behavior of the relativistic effects cannot be explained in terms of single-electron density at the origin and should be attributed to many-body effects.

Let us see now how Eqs. (4)–(6) will be modified if the many-body correction $C(Z,j,l)$ is included. Assuming the same value of $C(Z,j,l)$ for $p_{1/2}$ and $p_{3/2}$ states we have for the fine splitting

$$\Delta_{ls} = E(p_{3/2}) - E(p_{1/2}) \simeq -\frac{1}{2} E_n \frac{(Z\alpha)^2}{\nu(j+1/2)}. \quad (8)$$

For the mean energy of the $p$ electron instead of Eq. (5) we have

$$E(p) = E_n(p) + \left(2C - \frac{4}{3}\right)\Delta_{ls}. \quad (9)$$

With $C = 0.6$ the second term in Eq. (9) is numerically small. Hence, relativistic corrections move the $p_{1/2}$ and $p_{3/2}$ states in opposite directions, leaving the mean energy almost unchanged. Therefore the relativistic shift of the mean $s$-$p$ transition is mostly given by the energy shift of the $s$ state

$$\Delta(p-s) \simeq -\Delta(s_{1/2}). \quad (10)$$

The relative sizes of relativistic corrections are proportional to $Z^2$, so they are small in light atoms. Therefore we can constrain changes in $\alpha$ by comparing transition frequencies in heavy and light atoms. We stress that the most accurate and effective procedure includes all relativistic corrections and the analysis of all available lines (rather than the fine splitting within one multiplet only). We have not discussed here contribution of the Breit relativistic correction to the electron-electron interaction. It is not enhanced by the factor $Z^2$ and is much smaller than the contribution from spin-orbit interaction. Our numerical calculations have demonstrated that the contribution of the Breit interaction to the frequency of $s$-$p$ transition $\Delta(p-s)$ is indeed negligible.

### B. Relativistic many-body calculations

Accurate calculations of relativistic effects in atoms have been done using many-body theory which includes electron-electron correlations. We used a correlation-potential method [10] for atoms with one external electron above closed shells and a combined configuration interaction and many-body perturbation theory method [11] for atoms with several valence electrons. A relativistic Hartree-Fock (RHF) Hamiltonian was used in both cases to generate a complete set of single-electron orbitals. The values of the relativistic correc-

tions were obtained by repeating the calculations for different values of $\alpha$ in the RHF Hamiltonian.

The form of the single-electron wave function we use explicitly includes a dependence on the fine-structure constant $\alpha$,

$$\psi(\mathbf{r})_{njlm} = \frac{1}{r}\left(\begin{array}{c} f(r)_n \Omega(\mathbf{r}/r)_{jlm} \\ i\alpha g(r)_n \tilde{\Omega}(\mathbf{r}/r)_{jlm} \end{array}\right). \quad (11)$$

This leads to the following form of the RHF equations:

$$f_n'(r) + \frac{\kappa_n}{r} f_n(r) - [2 + \alpha^2(\epsilon_n - \hat{V})]g_n(r) = 0,$$

$$\quad (12)$$

$$g_n'(r) - \frac{\kappa_n}{r} g_n(r) + (\epsilon_n - \hat{V})f_n(r) = 0,$$

where $\kappa = (-1)^{l+j+1/2}(j+1/2)$ and $V$ is the Hartree-Fock potential:

$$\hat{V}f = V_d(r)f(r) - \int V_{\text{exch}}(r,r')f(r')dr'. \quad (13)$$

The nonrelativistic limit can be achieved by reducing the value of $\alpha$ to $\alpha = 0$.

For atoms or ions with one external electron above closed shells, the calculations begin with the $V^{N-1}$ approximation. A Hartree-Fock procedure is carried out initially for a closed-shell ion with the external electron removed. When convergence for the core is achieved, the states of the external electron are calculated in the field of the frozen core. The main reason for this approach is the simplicity of the perturbation theory for calculation of the correlation corrections. It is well known that correlations are very important in many-electron atoms and should be included in the calculations to obtain accurate results. We do this by means of many-body perturbation theory (MBPT) and a correlation-potential method [10].

The correlation potential $\hat{\Sigma}$ is defined as an operator which gives a correlation correction to the energy (ionization potential) of the valence electron

$$\delta\epsilon_a = \langle a|\hat{\Sigma}|a\rangle. \quad (14)$$

The expectation value here is taken over the single-particle wave function of the external (valence) electron. Thus $\hat{\Sigma}$ is another nonlocal operator which can be included in Eq. (13) by redefining the nonlocal potential

$$V_{\text{exch}}(r,r') \rightarrow V_{\text{exch}}(r,r') + \Sigma(r,r'). \quad (15)$$

Single-electron states of a valence electron calculated in a nonlocal potential (15) are often called Brueckner orbitals.

MBPT is used to calculate $\Sigma$. Perturbation expansion starts from the second order in residual Coulomb interaction. Dominating higher-order correlations can also be included by using the technique developed in Ref. [12]. However, we found that for the few-electron ions such as C IV and Si IV, second-order results are already of very high accuracy (see Table I). Therefore we decided that the accurate calculations of higher-order corrections are not needed.

TABLE I. Energy levels of C IV and Si IV with respect to the continuous spectrum limit (cm$^{-1}$).

| Ion | State | RHF | Brueckner | Experiment [a] |
|---|---|---|---|---|
| C IV | $2s_{1/2}$ | 519253 | 520082 | 520178 |
|  | $2p_{1/2}$ | 454054 | 455508 | 455694 |
|  | $2p_{3/2}$ | 453926 | 455337 | 455587 |
|  | $3d_{3/2}$ | 195196 | 195287 | 195298 |
|  | $3d_{5/2}$ | 195187 | 195277 | 195287 |
| Si IV | $3s_{1/2}$ | 360613 | 363840 | 364098 |
|  | $3p_{1/2}$ | 290073 | 292514 | 292808 |
|  | $3p_{3/2}$ | 289606 | 292036 | 292348 |
|  | $3d_{3/2}$ | 201807 | 203480 | 203721 |
|  | $3d_{5/2}$ | 201807 | 203472 | 203721 |

[a]Reference [27]; numbers are rounded to the last digit before the decimal point.

For some other atoms we introduce fitting parameters $f_v$ into the expression for the nonlocal potential in Eq. (13) to simulate the effect of higher-order correlations: $V_{\text{nonlocal}} = V_{\text{exch}} + f_v \Sigma$, where $v = s$, $p$ or $d$. The values for $f_s$, $f_p$ and $f_d$ are chosen to fit the experimental data for laboratory value $\alpha = 1/137.036$. In all cases the values of $f_v$ are close to unity. The same $f_v$ have been used for calculations with varying $\alpha$. This procedure works well because the accuracy of the results in the second order is already good and only a small correction is introduced by the fitting parameters.

For atoms with more than one external electron we use the combination of the configuration interaction method with many-body perturbation theory [11].

(1) As for single-electron-above-closed-shells atoms, we start calculations from the RHF method in $V^{N-1}$ approximation. However, this starting approximation does not correspond to a closed-shell system and needs to be further specified. We do this in a very simple way. The contribution of an open shell to the Hartree-Fock potential is calculated using the complete shell potential multiplied by the ''occupation'' factor $n/(2j+1)$, where $n$ is the actual number of electrons on that shell and $j$ is the total single-electron momentum. Single-electron basis states are calculated in this Hartree-Fock potential with one external electron removed ($V^{N-1}$ potential).

(2) All basis states are divided into core states and valence states. Core states are frozen and included into calculations only via the effective potential of the core. Valence states are used as a basis for the configuration interaction (CI) method. Note that the definition of the core at this stage does not necessarily coincide with the core in RHF calculations. For example, for Fe II $3d_{3/2}$ and $3d_{5/2}$ states are core states in the RHF procedure. But these states are also included into the configuration interaction, so they are valence states in the CI calculations.

(3) The effective Hamiltonian of the CI method is constructed. To include correlations between core and valence electrons we modify the effective Hamiltonian of the standard CI method by adding an extra operator $\Sigma$,

$$\hat{H}_{\text{eff}}^{\text{CI}} \to H_{\text{eff}}^{\text{CI}} + \hat{\Sigma}.$$

The operator $\Sigma$ consists of two parts. $\Sigma_1$ is the one-electron operator which describes the correlation interaction between a valence electron and the core. $\Sigma_1$ is very similar to the correlation potential $\Sigma$ in Eq. (15) which we used for atoms with one external electron above closed shells. $\Sigma_2$ is a two-particle operator which describes the effects of screening of the Coulomb interaction between valence electrons by the core electrons. It has been demonstrated in Ref. [11] that the core-valence correlations are very important and usually dominate over correlations between valence electrons. Thus it is more important to include $\Sigma$ than to achieve the completeness of the basis in the CI calculations.

(4) The standard CI technique is used to diagonalize the matrix of the effective CI Hamiltonian and obtain many-electron energies and wave functions. We need to apply this method to the atoms with many electrons in open shell. This can make configuration space and computation time very large. However, we do not need very high accuracy in the present calculations. Therefore, we have made a few simplifications to the method compared to Ref. [11]. The effect of screening ($\Sigma_2$) is usually much smaller than one-electron correlations with the core ($\Sigma_1$) and we neglect it. We also neglect subtracting diagrams in $\Sigma_1$ (see Ref. [11]) because there must be strong cancellations between screening and subtracting diagrams. Finally, we use a relatively small basis set with three to four single-electron basis states of each symmetry. This usually leads to a few hundred configurations. This small basis is not complete to high precision. However, the results are reasonably good because correlations with the core are included (see Table II). To simulate the effect of incompleteness of the basis and of the omitted diagrams we introduce fitting parameters for $\Sigma$, similar to what we did for atoms with one external electron. The results for Cr II presented in Table II illustrate the effects of core-valence correlations, correlations between valence electrons, and the effect of fitting. Note that only one fitting parameter was used to fit all energy levels.

There are two contributions to the relativistic energy shift. The first is the direct relativistic correction to the energy of a valence electron in the Hartree-Fock-Dirac equations (12). This correction can be found by varying $\alpha$ in Eq. (12) with fixed potential. There is also an indirect relativistic correction which appears because of the change of the core potential (including correlation potential) due to the relativistic effects in the core. Neither the correlation potential $\Sigma$ nor the standard Hartree-Fock potential depend on $\alpha$ explicitly. This dependence appears via the basis set of single-electron wave functions used to calculate both potentials since these wave functions had been obtained by solving Dirac-like equations (12). Full-scale calculations, repeated for different values of $\alpha$, were necessary to reveal this implicit relativistic behavior. The value of the indirect effect is not small and in some cases exceeds several times the value of the direct one. This indirect relativistic effect is essentially a many-body effect. It is responsible for the failure of the single-particle formula (3) which is unable to reproduce the value of the relativistic correction accurately.

### III. RESULTS AND DISCUSSION

To find the dependence of frequencies on $\alpha$ we use the following formula for the energy levels within one fine-structure multiplet:

TABLE II. Ionization potential and excitation energies of Cr II (cm$^{-1}$).

| State | RHF [a] | RHF + $\Sigma$ [b] | CI + $\Sigma$ [c] | CI + $f \times \Sigma$ [d] | Experiment [e] |
|-------|---------|--------------------|--------------------|-----------------------------|----------------|
| | | | Ionization potential | | |
| $3d^5\,6S_{5/2}$ | 125889 | 141067 | 137208 | 133815 | 133060 |
| | | | Excitation energies | | |
| $3d^4 4p\,^6F_{3/2}$ | 40230 | 52943 | 50233 | 46777 | 46905.52 |
| $3d^4 4p\,^6F_{5/2}$ | 40388 | 53125 | 50411 | 46949 | 47040.54 |
| $3d^4 4p\,^6F_{7/2}$ | 40606 | 53377 | 50655 | 47187 | 47227.50 |
| $3d^4 4p\,^6P_{3/2}$ | 42422 | 55171 | 51902 | 48466 | 48399.19 |
| $3d^4 4p\,^6P_{5/2}$ | 42562 | 55342 | 52067 | 48621 | 48491.39 |
| $3d^4 4p\,^6P_{7/2}$ | 42758 | 55581 | 52304 | 48844 | 48632.36 |

[a]Single-configuration approximation.
[b]As RHF but correlations with core electrons included in the second order.
[c]Configuration interaction for 343 relativistic configurations; correlations with core are also included.
[d]Screening parameter $f_d = 0.74$ has been set for correlations of $d$-valence electrons with the core to fit ionization potential and excitation energies.
[e]Reference [27].

$$E = E_0 + Q_1 \left[ \left( \frac{\alpha}{\alpha_l} \right)^2 - 1 \right] + Q_2 \left[ \left( \frac{\alpha}{\alpha_l} \right)^4 - 1 \right] + K_1 (\mathbf{LS}) \left( \frac{\alpha}{\alpha_l} \right)^2$$

$$+ K_2 (\mathbf{LS})^2 \left( \frac{\alpha}{\alpha_l} \right)^4. \qquad (16)$$

Here $E_0$, $Q_1$, and $Q_2$ describe the position of the configuration center, $K_1$ and $K_2$ describe the level splitting within one configuration, $L$ is the total orbital angular momentum, $S$ is the total electron spin, and $\alpha_l$ is the laboratory value of $\alpha$. We introduce an $(\mathbf{LS})^2$ term to describe deviations from the Lande interval rule. There are two sources of the $(\mathbf{LS})^2$ term: the second order in the spin-orbit interaction $[ \sim (Z\alpha)^4 ]$ and the first order in the Breit interaction ($\sim \alpha^2 = 5.3 \times 10^{-5}$).

The second-order spin-orbit interaction is larger for heavy atoms where we actually need to introduce the $(\mathbf{LS})^2$ term. Therefore we first fitted the experimental fine-structure intervals to find $K_1$ and $K_2$ (numerical calculations give close values of $K_1$ and $K_2$). Then we used numerical calculations for $\alpha = \sqrt{7/8}\,\alpha_l$ and $\alpha = \sqrt{3/4}\,\alpha_l$ to find the dependence of the configuration center on $\alpha$ (coefficients $Q_1$ and $Q_2$). It is convenient to represent the final results in the form

$$\omega = \omega_0 + q_1 x + q_2 y, \qquad (17)$$

where $q_1 = Q_1 + K_1(\mathbf{LS})$, $q_2 = Q_2 + K_2(\mathbf{LS})^2$, $x = (\alpha/\alpha_l)^2 - 1$, $y = (\alpha/\alpha_l)^4 - 1$, and $\omega_0 = E_0 + K_1(\mathbf{LS}) + K_2(\mathbf{LS})^2$ is an experimental energy of a particular state of the fine-structure multiplet. The parameters $\omega_0$, $q_1$, and $q_2$ for $E1$ transitions for many atoms and ions of astrophysical interest are presented in Table III.

One can use these data to fit absorption systems in quasar spectra in order to measure or place upper limits on any variation of $\alpha$. The maximum theoretical sensitivity comes from comparing the spectra of Fe II and Cr II since relativistic effects in both ions are large and have opposite sign. The effect here is about 20 times larger than the fine splitting for each of the ions.

An analysis of the theoretical data reveals some interesting tendencies in the behavior of the relativistic corrections apart from being proportional to $Z^2$.

(1) Within a series of one-electron orbitals of a given symmetry, the relativistic energy shift is largest for the lowest orbital and decreases for orbitals of higher energies. This trend is supported by the semiempirical consideration presented in Sec. I. The higher electron density in the vicinity of the nucleus gives larger relativistic effects. This also explains why the relativistic shift of the ground state energy is bigger when ionization potential is larger.

(2) When $\alpha$ is changing towards its nonrelativistic limit $\alpha = 0$, one-electron energies of $s$ and $p_{1/2}$ states move up while energies of $p_{3/2}$ and $d$ states move down. The relativistic shifts of $s$ and $d$ states tend to be large while the energy shifts of $p$ states are relatively small. Note that the single-particle consideration suggests that the relativistic shifts are large for $s$ and $p_{1/2}$ states and all energies move up when $\alpha$ is decreasing [see formulas (3)–(5)]. Accurate calculations give different behaviors due to indirect relativistic effects: relativistic corrections to the core orbitals change the electronic potential which in turn shifts the energy of the external electron. This effect is neglected in a naive single-particle formula. The direct effect dominates over the core change effect for $s$ states. For $p$ states these two effects are close in magnitude but opposite in sign. The core change effect dominates for $d$ states. Thus introduction of $C(Z,j,l)$ in Eq. (8) effectively takes into account the core change effect.

These tendencies are illustrated by the results presented in Table III. For example, the relativistic shifts of frequencies of $E1$ transitions are negative in Cr II and Ge II and positive for other atoms. This is because these transitions correspond to a $d$-$p$ one-electron transition in the case of Cr II and to a $p$-$s$ transition for Ge II while for the other atoms the transitions are of the $s$-$p$ type. The relativistic correction for Ge II is relatively small because the corresponding transition may be described as the transition from the ground $p$ orbital to excited $s$ orbital and because the relativistic corrections are small for both $p$ states and excited states. Another example is the sharp increase of the relativistic effect from Ca II to Cr II. This is due to the coherent effect of two factors: bigger $Z$ and bigger ionization potential for Cr II as compared to Ca II.

As is apparent from the analysis above one should expect the biggest relativistic shift for the $s$-$d$ (or $d$-$s$) transitions in

TABLE III. Dependence on $\alpha$ of the frequencies of the $E1$ atomic transitions of astronomic interest $(cm^{-1})$. Here $\omega = \omega_0 + q_1 x + q_2 y$ where $x = (\alpha/\alpha_l)^2 - 1$, $y = (\alpha/\alpha_l)^4 - 1$.

| $Z$ | Atom/ion | Ground state | | Upper states | | $\omega_0$ | $q_1$ | $q_2$ |
|---|---|---|---|---|---|---|---|---|
| 6 | C II | $2s^2 2p$ | $^2P^o_{1/2}$ | $2s2p^2$ | $^2D_{3/2}$ | 74932.617 [a] | 177 | 3 |
| | | | | $2s2p^2$ | $^2S_{1/2}$ | 96493.742 [a] | 171 | 3 |
| | | | | $2s2p^2$ | $^2P_{1/2}$ | 110625.1 [b] | 173 | $-3$ |
| | | | | $2s2p^2$ | $^2P_{3/2}$ | 110666.3 [b] | 217 | 3 |
| 6 | C IV | $1s^2 2s$ | $^2S_{1/2}$ | $1s^2 2p$ | $^2P_{1/2}$ | 64484.094 [a] | 108 | 8 |
| | | | | $1s^2 2p$ | $^2P_{3/2}$ | 64591.348 [a] | 231 | $-8$ |
| 7 | N V | $2s$ | $^2S_{1/2}$ | $2p$ | $^2P_{1/2}$ | 80463.211 [a] | 196 | $-4$ |
| | | | | $2p$ | $^2P_{3/2}$ | 80721.906 [a] | 488 | 2 |
| 8 | O I | $2p^4$ | $^3P_2$ | $2p^3 3s$ | $^3S_1$ | 76794.977 [a] | 130 | $-30$ |
| | | | | $2p^3 4s$ | $^3S_1$ | 96225.055 [a] | 140 | $-20$ |
| 12 | Mg I | $3s^2$ | $^1S_0$ | $3s3p$ | $^1P_1$ | 35051.277 [c] | 106 | $-10$ |
| 12 | Mg II | $3s$ | $^2S_{1/2}$ | $3p$ | $^2P_{1/2}$ | 35669.298 [c] | 120 | 0 |
| | | | | $3p$ | $^2P_{3/2}$ | 35760.848 [c] | 211 | 0 |
| 13 | Al III | $3s$ | $^2S_{1/2}$ | $3p$ | $^2P_{1/2}$ | 53682.330 [a] | 216 | 0 |
| | | | | $3p$ | $^2P_{3/2}$ | 53916.598 [a] | 464 | 0 |
| 14 | Si II | $3s^2 3p$ | $^2P^o_{1/2}$ | $3s3p^2$ | $^2D_{3/2}$ | 55309.352 [a] | 547 | $-6$ |
| 14 | Si IV | $2p^6 3s$ | $^2S_{1/2}$ | $2p^6 3p$ | $^2P_{1/2}$ | 71287.523 [a] | 362 | $-8$ |
| | | | | $2p^6 3p$ | $^2P_{3/2}$ | 71748.625 [a] | 766 | 48 |
| 20 | Ca I | $4s^2$ | $^1S_0$ | $4s4p$ | $^1P_1$ | 23652.305 [a] | 300 | 0 |
| 20 | Ca II | $3p^6 4s$ | $^2S_{1/2}$ | $3p^6 4p$ | $^2P_{1/2}$ | 25191.512 [a] | 192 | 16 |
| | | | | $3p^6 4p$ | $^2P_{3/2}$ | 25414.427 [a] | 420 | 16 |
| 24 | Cr II | $3d^5$ | $^6S_{5/2}$ | $3d^4 4p$ | $^6F_{3/2}$ | 46905.17 [d] | $-1624$ | $-25$ |
| | | | | $3d^4 4p$ | $^6F_{5/2}$ | 47040.35 [d] | $-1493$ | $-21$ |
| | | | | $3d^4 4p$ | $^6F_{7/2}$ | 47227.24 [d] | $-1309$ | $-18$ |
| | | | | $3d^4 4p$ | $^6P_{3/2}$ | 48398.941 [a] | $-1267$ | $-9$ |
| | | | | $3d^4 4p$ | $^6P_{5/2}$ | 48491.105 [a] | $-1168$ | $-16$ |
| | | | | $3d^4 4p$ | $^6P_{7/2}$ | 48632.125 [a] | $-1030$ | $-13$ |
| 25 | Mn II | $3d^5 4s$ | $^7S_3$ | $3d^5 4p$ | $^7P_2$ | 38366.184 [a] | 918 | 34 |
| | | | | $3d^5 4p$ | $^7P_3$ | 38543.086 [a] | 1110 | 19 |
| | | | | $3d^5 4p$ | $^7P_4$ | 38806.664 [a] | 1366 | 27 |
| 26 | Fe II | $3d^6 4s$ | $^6D_{9/2}$ | $3d^6 4p$ | $^6D^o_{9/2}$ | 38458.9871 [e] | 1449 | 2 |
| | | | | $3d^6 4p$ | $^6D^o_{7/2}$ | 38660.0494 [e] | 1687 | $-36$ |
| | | | | $3d^6 4p$ | $^6F_{11/2}$ | 41968.0642 [e] | 1580 | 29 |
| | | | | $3d^6 4p$ | $^6F_{9/2}$ | 42114.8329 [e] | 1730 | 26 |
| | | | | $3d^6 4p$ | $^6F_{7/2}$ | 42237.0500 [e] | 1852 | 26 |
| | | | | $3d^6 4p$ | $^6P_{7/2}$ | 42658.2404 [e] | 1325 | 47 |
| 30 | Zn II | $3d^{10} 4s$ | $^2S_{1/2}$ | $3d^{10} 4p$ | $^2P_{1/2}$ | 48480.992 [a] | 1445 | 66 |
| | | | | $3d^{10} 4p$ | $^2P_{3/2}$ | 49355.027 [a] | 2291 | 94 |
| 32 | Ge II | $4s^2 4p$ | $^2P_{1/2}$ | $4s^2 5s$ | $^2S_{1/2}$ | 62403.027 [a] | $-575$ | $-16$ |

[a]Morton, Ref. [26].
[b]Moore, Ref. [27].
[c]Pickering, Thorne, and Webb, Ref. [28].
[d]Sugar and Corliss, Ref. [29].
[e]Nave et al., Ref. [30].

heavy atoms. These transitions are not observed in quasar absorption systems but may be suitable for laboratory experiments. The natural linewidth for these transitions is very small. Furthermore, very precise measurements of the frequencies of many such transitions already exist since they are used as atomic optical frequency standards. We present in Table IV relativistic shifts of frequencies of some atomic transitions which are used or proposed as optical frequency standards. These include the strongly forbidden $E1$ transition in Ca I [13] and $E2$ transitions in Sr II [14], Yb II [15], and Hg II [16]. There are many other atoms which are being studied as possible frequency standards but which are not included in the table. These include Mg I [17], In II [18], Xe I [19], Ag I [20], etc. Note that the biggest relativistic effect is in Hg II. This is because of the $d$-$s$ transition and a high value of $Z$. This makes Hg II the most interesting candidate for a laboratory search for $\alpha$ variations.

The following limit of $\alpha$ variation was found in Ref. [7]:

TABLE IV. Relativistic shift of energies of some metastable states of atoms which are used as optical frequency standards (cm$^{-1}$).

| $Z$ | Atom/ion | Ground state | | Upper states | | $\omega_0$ | $q_1$ | $q_2$ |
|---|---|---|---|---|---|---|---|---|
| 20 | Ca I | $4s^2$ | $^1S_0$ | $4s4p$ | $^3P_1$ | 15210. | 230 | 0 |
| 38 | Sr II | $5s$ | $^2S_{1/2}$ | $4d$ | $^2D_{3/2}$ | 14555.90 | 2636 | 96 |
| | | | | $4d$ | $^2D_{5/2}$ | 14836.24 | 2852 | 160 |
| 70 | Yb II | $6s$ | $^2S_{1/2}$ | $5d$ | $^2D_{3/2}$ | 24332.69 | 9898 | 1342 |
| | | | | $5d$ | $^2D_{5/2}$ | 22960.80 | 8298 | 1570 |
| 80 | Hg II | $5d^{10}6s$ | $^2S_{1/2}$ | $5d^96s^2$ | $^2D_{5/2}$ | 35514.0 | $-36785$ | $-9943$ |
| | | | | $5d^96s^2$ | $^2D_{3/2}$ | 50552.0 | $-19377$ | $-12313$ |

$$\frac{\langle \dot{\alpha} \rangle}{\alpha} = +2.6 \pm 5.2 \times 10^{-16}. \qquad (18)$$

Assuming $\dot{\alpha}/\alpha = 10^{-15}$ one can get for the $5d^{10}6s\,^2S_{1/2} - 5d^96s^2\,^2D_{5/2}$ transition in Hg II

$$\dot{\omega} = 3 \ \text{Hz yr}^{-1},$$

which should be compared with the natural linewidth limit of 1.8 Hz [16].

There are also ongoing laboratory searches for variations of $\alpha$ using microwave atomic frequency standards (atomic clocks) (see, e.g., [22]). There are a number of microwave frequency standards which use ground state hyperfine structure (hfs) intervals of atoms or ions (see, e.g., review [23]). These include hfs of Rb, Cd$^+$, Cs, Ba$^+$, Yb$^+$, and Hg$^+$ [23]. Here again the biggest relativistic effects are in the Hg$^+$ ion. It is convenient to present the $\alpha$ dependence of hfs constants in a form similar to Eq. (17),

$$A_{\text{hfs}} = \left(\frac{\alpha}{\alpha_l}\right)^2 (A_0 + qx), \qquad (19)$$

where $A_0$ is the hfs constant for $\alpha = \alpha_l$. Its value for Hg$^+$ was recently measured to very high precision:

$$A_0(\text{Hg}^+) = 40\,507\,347\,996.841\,59(14)(41)\,\text{Hz}$$

[21]. Many-body calculations similar to the calculations of energies described above show that $q = 40\,500$ MHz for Hg II and $q = 956$ MHz for Cs I. Note that $A_0(^{133}\text{Cs}) = 2\,298\,157\,943$ Hz. This is the exact value because the frequency $9\,192\,631\,770$ Hz of the $6s \ F=3 - 6s \ F=4$ hfs transition in $^{133}$Cs, which is equal to $4A_0(6s)$, is used as a definition of the metric second.

Relative drifts in rates of atomic clocks based on Hg II and Cs will be

$$\frac{d}{dt}\ln\frac{A(\text{Hg})}{A(\text{Cs})} = \left(\frac{2q}{A_0}(\text{Hg}^+) - \frac{2q}{A_0}(\text{Cs})\right)\frac{\dot{\alpha}}{\alpha} = (2.30 - 0.83)\frac{\dot{\alpha}}{\alpha}$$

$$= 1.47\frac{\dot{\alpha}}{\alpha}.$$

This is in good agreement with estimates based on the Fermi-Segre formula [22]. The best sensitivity of various clock rate comparisons can be achieved when Hg$^+$ clocks are compared with a H maser [22] (parameter $q=0$ for H). Assuming again $\dot{\alpha}/\alpha = 10^{-15}$ yr$^{-1}$ we will get 2.3 $\times 10^{-15}$ yr$^{-1}$ for the frequency rate shift between H maser and Hg$^+$ clocks. Note that the ratio of hyperfine structure constants is also sensitive to the variation of nuclear magnetic $g$ factors which may appear due to variation of strong interaction.

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 cm$^{-1}$ above ground state. (This pair of levels was used to study parity nonconservation in Refs. [24,25].) 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). In the case of ''accidental'' degeneracy, the contribution of the relativistic correction to the frequency of the $E1$ transition in a heavy atom ($\sim 1000$ cm$^{-1}$) is compensated by the difference in the Coulomb interaction energies of the two configurations. However, if $\alpha$ varies with time, this compensation will eventually disappear. Thus we have a correction $\sim 1000$ cm$^{-1}[(\alpha/\alpha_l)^2 - 1]$ to the very small ($< 0.01$ 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. In the case of ''accidentally'' degenerate levels belonging to different electron terms in a molecule one can have enhanced effects of the change of both $\alpha$ 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. The problem in these degenerate level cases is to find a transition with a small natural width.

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