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 provide a powerful tool for measuring these variations. In the present paper we demonstrate that high sensitivity to variation of the fine structure constant $\alpha$ can be obtained by comparing cosmic and laboratory spectra of the Ni II ion. Relativistic effects in Ni II reveal many interesting features. The Ni II spectrum exhibits avoided level crossing phenomenon under variation of $\alpha$ and the intervals between the levels have strong nonlinear dependencies on relativistic corrections. The values of the transition frequency shifts, due to the change of $\alpha$, vary significantly from state to state including change of the sign. This enhances the sensitivity to the variation of $\alpha$ and reduces possible systematic errors. The calculations of $\alpha$-dependence of the nickel ion spectral lines that are detectable in quasar absorption spectra have been performed using a relativistic configuration interaction method.

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Possible variations of the fundamental physical constants in the expanding Universe are currently of particular interest because of the implications of unified theories, such as string theory and M-theory. They predict that additional compact dimensions of space exist. The “constants” seen in our three-dimensional subspace of the theory will vary according to any variation 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 in astronomical spectra. 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 $\frac{me^4}{\hbar^2}$. In the non-relativistic 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 red shift parameter $z$ ($1 + z = \frac{\omega'}{\omega}$, $\omega'$ is the red-shifted 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].

In our previous works [6,7] we have demonstrated that high sensitivity to the change of $\alpha$ can be achieved by comparing transition frequencies of heavy and light atoms. The results of our calculations for Fe II and Mg II have been used in Ref. [8] where the results of the search for $\alpha$-variation have been presented. Applied to a sample of 30 absorption systems, spanning red-shifts $0.5 < z < 1.6$, obtained with the Keck I telescope, the limits on variations in $\alpha$ over a wide range of epochs have been derived. For the whole sample $\Delta \alpha/\alpha = -1.1 \pm 0.4 \times 10^{-5}$. Whilst these results are consistent with a time-varying $\alpha$, further work is required to explore possible systematic errors in the data, although careful searches have so far not revealed any
The obvious way to test these results and further improve sensitivity is to include new atoms and spectral lines with different frequencies and different dependence on $\alpha$. It would be especially attractive to have lines with large relativistic shifts of the opposite signs since the opposite signs of the shifts lead to the suppression of the most dangerous systematic errors. The shift of lines produced by systematic errors “does not know” about the signs of the relativistic shifts. Therefore, it is easier to eliminate systematic errors when the signs are different.

In the present paper we demonstrate that the Ni II ion has a very interesting spectrum which possesses these desirable properties (see Table I). It is also very important that there are several strong Ni II lines observed in the quasar absorption spectra.

Note that we present all results in this paper assuming that the atomic unit of energy $\frac{m_e c^2}{\hbar^2}$ is constant (since any variation of this unit will be absorbed in the determination of the redshift parameter $z$).

II. THEORY AND RESULTS

Relativistic energy shift for a particular valence electron can be approximately described by the equation [7]

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

where $\nu$ is the principal quantum number ($E_n = -1/2\nu^2$) and $C(Z,j,l)$ accounts for the many-body effects. In many cases $C(Z,j,l) \approx 0.6$, however the accurate value of $C(Z,j,l)$ can only be obtained from the many-body calculations. Formula (1) accounts for the relativistic effects which are included into the single-electron Dirac equation. Note that they cannot be reduced to the spin-orbit interaction. For example, as is evident from the formula (1) the energy shift is large for $s$-electrons which have no spin-orbit interaction at all. Moreover, the spin-orbit interaction doesn’t even dominate in the relativistic energy shift. However, only the spin-orbit interaction can be found from the analysis of the experimental fine structure splitting while other relativistic effects remain “hidden”. Note that the
Coulomb integrals which determine splitting between different multiplets in many-electron states also contain relativistic corrections.

Thus, the analysis of the experimental atomic spectra does not provide sufficient information about relativistic effects in transition frequencies in atoms. For an atom with one external electron above closed shells one can obtain an approximate relativistic frequency shift by applying formula (1) to both upper and lower states of the transition. For a many-electron atom like Ni II this procedure is too inaccurate. Therefore the only way to get the results is to perform \textit{ab initio} relativistic calculations. However, the accuracy of the \textit{ab initio} results can still be improved by semiempirical fitting of the experimental data. This roughly describes the procedure used in the present work.

It is convenient to present the shift of frequency of an atomic transition under variation of $\alpha$ in the form

$$
\omega = \omega_0 + Q_1 x, \tag{2}
$$

where $x = (\alpha/\alpha_l)^2 - 1$, $\alpha_l$ is the laboratory value of the fine structure constant ($\alpha_l = 1/137.036$), and $\omega_0$ is the experimental value for frequency at $\alpha = \alpha_l$. Formula (2) is accurate in the vicinity of $\alpha = \alpha_l$. The purpose of the calculations is to determine the coefficients $Q_1$. This can be done by small variation of $\alpha$ in the vicinity of $\alpha_l$:

$$
Q_1 \approx \frac{\omega(\delta x) - \omega(-\delta x)}{2\delta x}. \tag{3}
$$

where $\omega$ are the calculated values of the frequencies. The lines of Ni II observed in quasar absorption spectra correspond to the transitions between ground state and three states of the $3d^84p$ configuration: $^2F_{7/2}(E = 57080\text{cm}^{-1})$, $^2D_{5/2}(E = 57420\text{cm}^{-1})$, $^2F_{5/2}(E = 58493\text{cm}^{-1})$. Energies and $g$-factors of these and other lowest odd states of Ni II are presented in Table I. One can see from the data that fine structure multiplets of Ni II sometimes overlap. In particular, the center of the $^2F$ doublet lies below the center of the $^2D$ doublet. However, the state $^2F_{5/2}$ has higher energy than the $^2D_{5/2}$. This means that if these energies are considered as functions of $\alpha^2$ there must be a level (pseudo)crossing somewhere between
\(\alpha = 0\) and \(\alpha = \alpha_l\). Note that the assignment of a particular state to a specific fine structure multiplet is best indicated by the value of their \(g\)-factors.

Another state of interest, \(2^2F_{7/2}\) is close to the state \(2^2G_{7/2}\) of a different doublet. Although the values of energies and \(g\)-factors of these two states indicate that no level crossing takes place between \(\alpha = 0\) and \(\alpha = \alpha_l\), \textit{ab initio} calculations show that such crossing happens in the vicinity of \(\alpha = \alpha_l\) (for \(\alpha > \alpha_l\)). This level crossing phenomenon makes calculations of the relativistic energy shifts for Ni II very difficult. Note that \(Q_1\) the coefficients (see eq. (3)) are the slopes of the curve \(E(\alpha^2)\) at \(\alpha = \alpha_l\). This slope usually changes sign at the point of the minimal distance between the levels (the level (pseudo)crossing point). Therefore, the values of \(Q_1\) are very sensitive to the position of the level crossing. On the other hand, the accuracy of \textit{ab initio} calculations is limited by the incompleteness of the basis set caused by the large number of valence electrons. Therefore, some approximations have to be made. Unfortunately, the positions of the level crossings and the \(Q_1\) coefficients vary significantly if we use different approximations. However, the energies and fine structure intervals are much less affected. In particular, the results of calculations are very stable for the center energies of the fine structure multiplets. Therefore, to obtain accurate results for \(Q_1\) we have adopted a calculation scheme which is a combination of the \textit{ab initio} calculations with a semi-empirical fitting. Firstly, we perform the \textit{ab initio} calculations using the Hartree-Fock and configuration interaction methods. Then, to improve the accuracy, we diagonalize the Hamiltonian (configuration interaction) matrix for a few close states. The matrix elements are considered as fitting parameters chosen to fit both the theoretical energy variation as a function of \(\alpha\) in the interval \(0 < \alpha < \alpha_l\) and the experimental energies and \(g\)-factors at \(\alpha = \alpha_l\). We consider this scheme in more detail below.

For \textit{ab initio} calculations we use the relativistic Hartree-Fock (RHF) and configuration interaction (CI) methods. We used a form of the single-electron wave function which explicitly includes a dependence on the fine structure constant \(\alpha\).
\[ \psi(r)_{njlm} = \frac{1}{r} \left( \begin{array}{c} f(r) \Omega(r/r)_{jlm} \\ i\alpha g(r) \tilde{\Omega}(r/r)_{jlm} \end{array} \right) \] 

(4)

This leads to the following form of the RHF equations

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

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

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

(6)

The non-relativistic limit can be achieved by reducing the value of \(\alpha\) to \(\alpha = 0\).

The ground state configuration of Ni II is \(3d^9\). This is an open-shell system and the RHF approximation needs to be further specified. We presented the contribution of the \(3d\) sub-shell to the Hartree-Fock potential as it was filled \((3d^{10})\) and then subtracted from the direct part of the potential a spherically symmetric contribution of one \(3d_{5/2}\) electron. The exchange part of the potential remained unchanged. The single-electron states \(4s, 4p_{1/2}\) and \(4p_{3/2}\) are calculated by removing a contribution of another \(3d_{5/2}\) electron from the direct Hartree-Fock potential.

We carry out CI calculations for 9 external electrons with all core states below \(3d\) being frozen. In this case the CI Hamiltonian has the form

\[ \hat{H}^{CI} = \sum_{i=1}^{9} \hat{h}_{1i} + \sum_{i<j}^{9} \frac{e^2}{r_{ij}} \] 

(7)

where \(\hat{h}_1\) is the one-electron part of the Hamiltonian.

The Hamiltonian (7) does not include important effects of correlations between the core and valence electrons (see, e.g. [10]). These correlations can be considered as consisting of two different effects. One effect is the correlation interaction of a particular electron with the core electrons (polarization of the core by an external electron). Another effect is screening of the Coulomb interaction between the valence electrons by the core electrons.
The core polarization effect affects mostly the single-particle energies (ionization potentials) of Ni II. However, the intervals between the excited many-body levels are not very sensitive to these correlations. Therefore, these correlations are not so important for the accurate calculations of $Q_1$ and we neglected them. Screening of the Coulomb interaction affects the interval between energy levels very strongly. We include the screening in a semiempirical way by introducing screening factors $f_k$. The factors are introduced in such a way that all Coulomb integrals of a definite multipolarity $k$ in the CI calculations are multiplied by the same numerical factors $f_k$. The values of the $f_k$ are chosen to fit experimental values for the intervals between states of interest listed in the beginning of this section. It turns out that the best fit is achieved at $f_1 = 0.75$, $f_2 = 0.9$ and $f_k = 1$ for all other values of $k$. The results for energy levels and $g$-factors calculated in this approximation are presented in Table I. Fig. 1 presents the energies of the $^4F_{5/2}$, $^2F_{5/2}$, $^2D_{5/2}$, $^4F_{7/2}$, $^2G_{7/2}$ and $^2F_{7/2}$ as functions of $\alpha$. One can see the level (pseudo)crossing at $(\alpha/\alpha_l)^2 = 0.3$ for the $^2F_{5/2}$ and $^2D_{5/2}$ states and at $(\alpha/\alpha_l)^2 = 0.9$ for the $^2G_{7/2}$ and $^2F_{7/2}$ states. Note that the experimental data for the energies and $g$-factors of the pair of states with $J = 9/2$ suggest that there is no level crossing in the interval $0 < \alpha < \alpha_0$. This is an indication that we slightly overestimated the relativistic effects in our ab initio calculations. Therefore, we varied the magnitude of the relativistic effects to fit the fine structure. The best fit is found for the relativistic corrections reduced by the factor 0.8. This reduction of the relativistic effects also gives the correct order of the levels with $J = 9/2$ (no level crossing for $\alpha < \alpha_l$).

As can be seen from Table I, the calculated fine structure, the intervals between the levels of the same $J$ and the $g$-factors are reasonably good. However, the coefficients $Q_1$ are quite sensitive to the position of the level crossing. Also, we miss a great part of the correlations between the valence electrons by restricting our basis set to just five single-electron states: $3d_{3/2}$, $3d_{5/2}$, $4s_{1/2}$, $4p_{1/2}$ and $4p_{3/2}$. Therefore, to achieve high accuracy in $Q_1$ we should make one more step. We vary and diagonalize the matrix of the level interaction to fit all available experimental data for the energy levels and $g$-factors. Three close states, as presented in Fig. 1, are included into the diagonalization procedure for both $J = 5/2$ and
\( J = 7/2 \) states. It is convenient to present the interaction matrix in the following form

\[
v_{ij} = e_i \delta_{ij} + q_{ij} \xi (\alpha/\alpha_l)^2.
\] (8)

Coefficients \( q_{ij} \) (at \( \xi = 1 \)) are chosen to fit the calculated behavior of the energies between \( \alpha = 0 \) and \( \alpha = \alpha_l \) as presented in Fig. 1. Let us remind the reader that the information about this behavior cannot be extracted from the experimental data and can only be obtained from \textit{ab initio} calculations. Energies \( e_i \) and the scaling factor for the relativistic effects \( \xi \) are chosen to fit the experimental energies and \( g \)-factors at \( \alpha = \alpha_l \).

It is also important to estimate the uncertainties for the calculated values of the \( Q_1 \) coefficients. To start with, we have performed the calculations by fitting only two close levels (instead of three levels) and compared the results for \( Q_1 \) with the three-level calculations. Then we did several fittings by varying the relative weight factors in the simultaneous fits of the energy levels and \( g \)-factors. In fact, we minimised the value of \( a \sum (\Delta E/E)^2 + (1 - a) \sum (\Delta g/g)^2 \) with the different weight factors \( a \). Finally, we performed the fitting procedures with the different limitations on the values of \( e_i \) and \( \xi \) to keep them close to the results of \textit{ab initio} calculations. We found that the results for \( Q_1 \) are reasonably stable and estimated uncertainties using the spread of these results.

The best fitting parameters together with fitted energies and \( g \)-factors are presented in Table 2. All fitted values are very close to the experimental results presented in Table 1.

The results for the relativistic energy shifts for the states of interest are

\[
^2F_{7/2} : \omega = 57080.373(4) - 300(200)x \\
^2D_{5/2} : \omega = 57420.013(4) - 700(200)x \\
^2F_{5/2} : \omega = 58493.071(4) + 800(200)x
\]

The estimated errors are presented in parentheses, \( x = (\alpha/\alpha_l)^2 - 1 \). The precise values of \( \omega_0 \) are presented in Ref. [12]. These expressions have been used in Ref. [13] to search for the variation of \( \alpha \).
III. CONCLUSION

It is instructive to compare the relativistic energy shifts for Ni II with those of other elements calculated earlier [7]. The order of magnitude of the effect for Ni II is the same as for its neighbor in the periodic table, Fe II [7]. However all energy shifts for Fe II are positive and close in value. This is because all the corresponding transitions are $s - p$ transitions and the values of the relativistic energy shift is dominated by the contribution of the $s$-electron. The close values of the relativistic shifts for all frequencies in Fe II makes it inefficient to use just these frequencies alone in the search for the variation of $\alpha$. This is because all possible variation of $\alpha$ will be absorbed by determination of the red-shift parameter $z$. For this reason we proposed in Refs. [7] and [6] to compare energy shifts in heavy elements, like iron, with the absorption spectrum of light elements from the same gas cloud. This was first done for the Fe II and Mg II spectra in Ref. [8]. The relativistic energy shift in Mg II is about ten times smaller than that in Fe II. This allowed us to use the transitions in Mg II as an “anchor” which does not change under variation of $\alpha$. Another possibility is to compare absorption spectra of elements in which the effect is large and opposite in sign, Fe II and Cr II for example [6]. In contrast to Fe II and other elements considered in Ref. [6], Ni II does not need such an anchor. Since the value of the relativistic shift varies strongly from state to state – including change of sign – both red-shift parameter and variation of $\alpha$ can be determined by comparing shifts of different lines of Ni II alone. This presents a new relatively simple and convenient way to study possible variation in the fine structure constant in the absorption spectra of distant quasars. Consideration of only one element with shifts of opposite sign should allow one to substantially reduce systematic errors.

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REFERENCES


[5] 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).


TABLE I. Lowest odd levels of Ni II (configuration 4d\(^8\)4p); energies, fine structure (cm\(^{-1}\)) and \(g\)-factors.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy(^a)</th>
<th>Interval(^a)</th>
<th>(g_{exp})(^a)</th>
<th>(g_{nr})(^b)</th>
<th>Energy(^c)</th>
<th>Interval(^c)</th>
<th>(g_{calc})(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^4)D(_{7/2})</td>
<td>51558.1</td>
<td></td>
<td>1.420</td>
<td>1.429</td>
<td>58594</td>
<td></td>
<td>1.4247</td>
</tr>
<tr>
<td>(^4)D(_{5/2})</td>
<td>52738.6</td>
<td>-1180.5</td>
<td>1.356</td>
<td>1.371</td>
<td>59826</td>
<td>-1232</td>
<td>1.3636</td>
</tr>
<tr>
<td>(^4)D(_{3/2})</td>
<td>56635.1</td>
<td>-896.5</td>
<td>1.186</td>
<td>1.200</td>
<td>60757</td>
<td>-923</td>
<td>1.1917</td>
</tr>
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<td>(^4)D(_{1/2})</td>
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<td>-0.005</td>
<td>0.0</td>
<td>61318</td>
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<td>0.0034</td>
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<td>1.305</td>
<td>1.273</td>
<td>60634</td>
<td></td>
<td>1.2725</td>
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<tr>
<td>(^4)G(_{9/2})</td>
<td>53365.2</td>
<td>131.6</td>
<td>1.156</td>
<td>1.172</td>
<td>61009</td>
<td>-375</td>
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<td>(^4)G(_{7/2})</td>
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<td>(^4)G(_{5/2})</td>
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<td>-756.1</td>
<td>0.616</td>
<td>0.571</td>
<td>62542</td>
<td>-719</td>
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<tr>
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<td>1.3042</td>
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<td>1.154</td>
<td>1.143</td>
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<tr>
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<td>0.857</td>
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<td>-1429</td>
<td>0.8030</td>
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\(^a\)Reference [11]

\(^b\)Non-relativistic value for \(g\)-factors

\(^c\)This work’s calculations
<table>
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<tr>
<th>$n$</th>
<th>$\epsilon_n$</th>
<th>$q_{1n}$</th>
<th>$q_{2n}$</th>
<th>$q_{3n}$</th>
<th>State</th>
<th>$E(\alpha = \alpha_l)$</th>
<th>$g(\alpha = \alpha_l)$</th>
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<td>1</td>
<td>55678</td>
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<td>268.63</td>
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<td>805.94</td>
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<td>3</td>
<td>58195</td>
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<td>$^2!F_{5/2}$</td>
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<td>$J = 5/2, \xi = 0.6806$</td>
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<tr>
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<td>55513</td>
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<td>$J = 7/2, \xi = 0.7151$</td>
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FIG. 1. Energy levels of Ni II with $J = 2.5$ (dashed line) and $J = 3.5$ (solid line) as functions of $\alpha$. Six states participating in the semi-empirical matrix diagonalization are shown.