Relativistic effects in Ni II and the search for variation of the fine-structure constant

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(Received 10 August 1999; revised manuscript received 11 October 2000; published 19 March 2001)

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 toward distant quasars provides a powerful tool for measuring these variations. In the present paper we demonstrate that high sensitivity to variation of the fine-structure constant α 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 crossings under variation of α 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 α, vary significantly from state to state including changes of sign. This enhances the sensitivity to the variation of α and reduces possible systematic errors. Calculations of the α dependence of the nickel ion spectral lines that are detectable in quasar absorption spectra have been performed using a relativistic configuration interaction method.

DOI: 10.1103/PhysRevA.63.042509 PACS number(s): 31.30.Jv, 06.20.Jr, 95.30.Dr

I. INTRODUCTION

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 that intersect the sight lines toward 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 $me^4/\hbar^2$. 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 $(1+z=\omega/\omega'$, where ω' is the redshifted frequency of the atomic transition and ω 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 α^2, where $\alpha=e^2/\hbar c$ is the fine-structure constant [5].

In our previous work [6,7] we have demonstrated that high sensitivity to the change of α can be achieved by comparing transition frequencies of heavy and light atoms. The results of our calculations for Fe II and Mg II were used in Ref. [8], where the results of a search for α variation were presented. Applied to a sample of 30 absorption systems, spanning redshifts $0.5<z<1.6$, obtained with the Keck I telescope, the limits on variation in α over a wide range of epochs have been derived. For the whole sample $\Delta\alpha/\alpha=-(1.1\pm0.4)\times10^{-5}$. Whilst these results are consistent with a time-varying α, further work is required to explore possible systematic errors in the data, although careful searches have so far not revealed any [9]. The obvious way to test these results and further improve sensitivity is to include new atoms and spectral lines with different frequencies and different dependences on α. It would be especially attractive to have lines with large relativistic shifts of 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 that 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 $me^4/\hbar^2$ is constant (since any variation of this unit will be absorbed in the determination of the redshift parameter z).

II. THEORY AND RESULTS

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

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

where ν 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 $C(Z,j,l)\simeq0.6$; however, the accurate value of $C(Z,j,l)$ can be obtained only from many-body calculations. Formula (1) accounts for the relativistic effects that are included in the single-electron Dirac equation. Note that they cannot be reduced to the spin-orbit interaction. For example, as is evident from formula (1), the energy shift is large for *s* electrons, which have no spin-orbit interaction at all. Moreover, the spin-orbit interaction does not dominate even in the relativistic energy shift. However, only the spin-orbit interaction

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

State	Energy [a]	Interval [a]	g_{expt} [a]	g_{nr} [b]	Energy [c]	Interval [c]	g_{calc} [c]
$^4D_{7/2}$	51558.1		1.420	1.429	58594		1.4247
$^4D_{5/2}$	52738.6	−1180.5	1.356	1.371	59826	−1232	1.3636
$^4D_{3/2}$	56635.1	−896.5	1.186	1.200	60757	−923	1.1917
$^4D_{1/2}$	54176.1	−541.0	−0.005	0.0	61318	−561	0.0034
$^4G_{11/2}$	53496.8		1.305	1.273	60634		1.2725
$^4G_{9/2}$	53365.2	131.6	1.156	1.172	61009	−375	1.1892
$^4G_{7/2}$	54262.7	−897.5	1.02	0.984	61823	−814	1.0153
$^4G_{5/2}$	55018.8	−756.1	0.616	0.571	62542	−719	0.6049
$^4F_{9/2}$	54557.3		1.26	1.333	62228		1.3042
$^4F_{7/2}$	55417.9	−860.6	1.184	1.238	63138	−910	1.2005
$^4F_{5/2}$	56075.2	−657.3	0.985	1.029	63838	−700	1.0002
$^4F_{3/2}$	56424.6	−349.4	0.412	0.400	64259	−429	0.4153
$^2G_{9/2}$	55300.0		1.152	1.111	63712		1.1222
$^2G_{7/2}$	56371.6	−1071.6	0.940	0.889	65191	−1479	0.9356
$^2F_{7/2}$	57080.3		1.154	1.143	65798		1.1077
$^2F_{5/2}$	58493.0	−1412.7	0.946	0.857	67469	−1671	0.9618
$^2D_{5/2}$	57419.7		1.116	1.200	66113		1.1022
$^2D_{3/2}$	58705.6	−1285.9	0.795	0.800	67542	−1429	0.8030

[a]Reference [11].
[b]Nonrelativistic value for g factors.
[c]This work's calculations.

can be found from 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, 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 *ab initio* relativistic calculations. However, the accuracy of the *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 α in the form

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

where $x=(\alpha/\alpha_l)^2-1$, α_l is the laboratory value of the fine-structure constant ($\alpha_l=1/137.036$), and ω_0 is the experimental value for the 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 variations of α in the vicinity of α_l:

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

where ω are the calculated values of the frequencies. The lines of Ni II observed in quasar absorption spectra correspond to transitions between the ground state and three states of the $3d^8 4p$ configuration: $^2F_{7/2}$ ($E=57\,080$ cm^{-1}), $^2D_{5/2}$ ($E=57\,420$ cm^{-1}), and $^2F_{5/2}$ ($E=58\,493$ cm^{-1}). Energies and g factors of these and the 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 $^2D_{5/2}$. This means that if these energies are considered as functions of α^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 values of their g factors.

Another state of interest, $^2F_{7/2}$, is close to the state $^2G_{7/2}$ 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 $\alpha=\alpha_l$, *ab initio* calculations show that such a 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 the coefficients Q_1 [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 *ab initio* calculations is limited by the incompleteness of the basis set caused by the large number of valence electrons. Therefore, some approxima-

tions 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 that is a combination of the *ab initio* calculations with a semiempirical fitting. First, we perform the *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 α 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 *ab initio* calculations we use the relativistic Hartree-Fock (RHF) and configuration interaction (CI) methods. We use a form of the single-electron wave function that explicitly includes a dependence on the fine-structure constant α,

$$\psi(\mathbf{r})_{njlm}=\frac{1}{r}\begin{pmatrix} f(r)_n\Omega(\mathbf{r}/r)_{jlm} \\ i\alpha g(r)_n\tilde{\Omega}(\mathbf{r}/r)_{jlm}\end{pmatrix}. \tag{4}$$

This leads to the following form of the RHF equations:

$$f_n'(r)+\frac{\kappa_n}{r}f_n(r)-[2+\alpha^2(\epsilon_n-\hat{V})]g_n(r)=0, \tag{5}$$

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

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

$$\hat{V}f=V_d(r)f(r)-\int V_{exch}(r,r')f(r')dr'. \tag{6}$$

The nonrelativistic limit can be achieved by reducing the value of α 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 $3d$ subshell to the Hartree-Fock potential as it was filled ($3d^{10}$) and then subtracted from the direct part of the potential the 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 the contribution of another $3d_{5/2}$ electron from the direct Hartree-Fock potential.

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

$$\hat{H}^{CI}=\sum_{i=1}^{9}\hat{h}_{1i}+\sum_{i<j}^{9}\frac{e^2}{r_{ij}}, \tag{7}$$

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

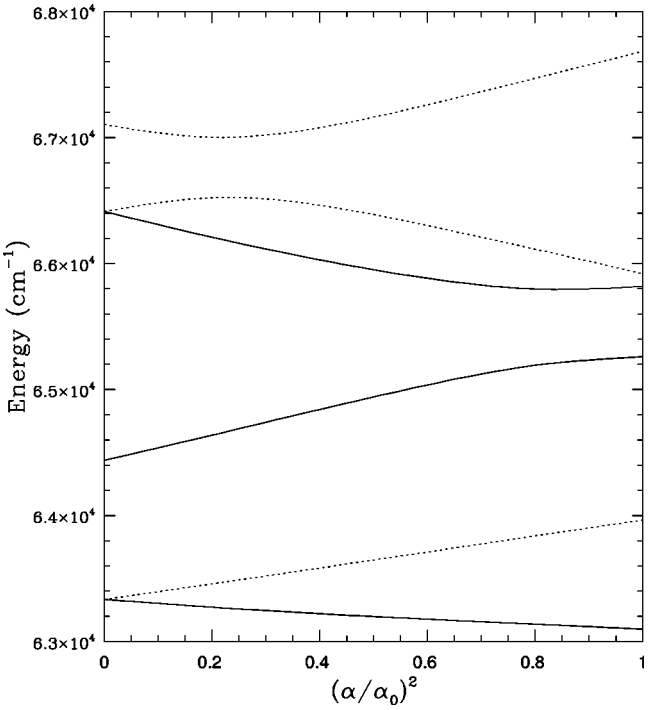

FIG. 1. Energy levels of Ni II with $J=2.5$ (dashed line) and $J=3.5$ (solid line) as functions of α. Six states participating in the semiempirical matrix diagonalization are shown.

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 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 at 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. Figure 1 presents the energies of $^4F_{5/2}$, $^2F_{5/2}$, $^2D_{5/2}$, $^4F_{7/2}$, $^2G_{7/2}$, and $^2F_{7/2}$ as functions of α. 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

TABLE II. Fitting parameters and fitted energies and g factors for the states of most interest of Ni II. Units for energies and q_{ij} are cm^{-1}.

n	e_n	q_{1n}	q_{2n}	q_{3n}	State	$E(\alpha=\alpha_l)$	$g(\alpha=\alpha_l)$
		$J=5/2, \quad \xi=0.6806$					
1	55678	650.41	268.63	148.21	$^4F_{5/2}$	56103	1.028
2	57705	268.63	805.94	758.62	$^2D_{5/2}$	57382	1.111
3	58195	148.21	758.62	−746.05	$^2F_{5/2}$	58577	0.945
		$J=7/2, \quad \xi=0.7151$					
1	55745	−221.58	248.78	121.67	$^4F_{7/2}$	55513	1.118
2	55184	248.78	1064.33	272.29	$^2G_{7/2}$	55986	0.944
3	58046	121.67	272.29	−915.07	$^2F_{7/2}$	57424	1.138

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 if 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 correlation 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 take 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 in the diagonalization procedure for both $J=5/2$ and $J=7/2$ states. It is convenient to present the interaction matrix in the form

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

The 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 information about this behavior cannot be extracted from the experimental data and can be obtained only from *ab initio* calculations. The energies e_i and the scaling factor for the relativistic effects ξ 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 minimized the value of $a\Sigma(\Delta E/E)^2+(1-a)\Sigma(\Delta g/g)^2$ with different weight factors a. Finally, we performed the fitting procedures with the different limitations on the values of e_i and ξ to keep them close to the results of *ab initio* calculations. We found that the results for Q_1 are reasonably stable and estimated uncertanties using the spread of these results.

The best fitting parameters together with fitted energies and g factors are presented in Table II. All fitted values are very close to the experimental results presented in Table I.

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

$$\omega=\begin{cases} 57\,080.373(4)-300(200)x, & {}^2F_{7/2}, \\ 57\,420.013(4)-700(200)x, & {}^2D_{5/2}, \\ 58\,493.071(4)+800(200)x, & {}^2F_{5/2}. \end{cases}$$

The estimated errors are presented in parentheses; $x=(\alpha/\alpha_l)^2-1$. The precise values of ω_0 are presented in Ref. [12]. These expressions were used in Ref. [13] to search for the variation of α.

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 value 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 make it inefficient to use just these frequencies alone in the search for the variations of α. This is because all possible variations of α will be absorbed by determination of the redshift 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 done for 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'' that does not change under variation of α. 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 the redshift parameter and the variation of α can be determined by comparing shifts of different lines of Ni II alone. This presents a 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 reduce systematic errors substantially.

ACKNOWLEDGMENT

This work was supported by the Australian Research Council.

[1] W. 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] D. A. Varshalovich and A. Y. Potekhin, Space Sci. Rev. **74**, 259 (1995).
[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).
[6] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. Lett. **82**, 888 (1999).
[7] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. A **59**, 230 (1999).
[8] J. K. Webb, V. V. Flambaum, C. W. Churchill, M. J. Drinkwater, and J. D. Barrow, Phys. Rev. Lett. **82**, 884 (1999).
[9] M. T. Murphy, J. K. Webb, V. V. Flambaum, C. W. Churchill, and J. X. Prochaska (unpublished).
[10] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).
[11] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, DC, 1958), Vol. III.
[12] J. C. Pickering, A. P. Thorne, J. E. Murray, U. Litzén, and J. K. Webb (unpublished).
[13] M. T. Murphy, J. K. Webb, V. V. Flambaum, V. A. Dzuba, C. W. Churchill, J. X. Prochaska, J. D. Barrow, and A. M. Wolfe (unpublished).