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Relativistic effects in two valence-electron atoms and ions and the search for variation of the fine-structure constant

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We perform accurate calculations of the dependence of transition frequencies in two-valence-electron atoms and ions on a variation of the fine-structure constant, $\alpha = e^2/\hbar c$. The relativistic Hartree-Fock method is used with many-body perturbation theory and configuration interaction methods to calculate transition frequencies. The results are to be used in atomic-clock-type laboratory experiments designed to test whether α varies in time.

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I. INTRODUCTION

Theories unifying gravity with other interactions allow for the possible variation of physical constants (see, e.g., [1–3]). A recent analysis of quasar absorption spectra suggests that the fine-structure constant α might vary in space-time [4–6]. There is an intensive search for alternative ways to test whether α is varying. One of the very promising methods to study the local present-day variation of fundamental constants in time involves the use of atomic clocks. In particular, optical atomic clock transitions are suitable to study the possible variation of the fine-structure constant. This is because the ratio of the frequencies of the optical transitions depend on α alone, while the frequencies of the hyperfine transitions also depend on the nuclear magnetic moments and the electron-proton mass ratio.

Laboratory measurements involve measuring how the difference between two frequencies changes with time. To relate a measurement of the change between two frequencies to a change in α, the relativistic energy shifts are needed. The relativistic energy shift describes how a level moves as α varies. Two transition frequencies with very different relativistic energy shifts are the most desirable candidates for precision experiments as they will have the largest relative frequency shift between them.

The best limit on the local present-day variation of the fine-structure constant published to date was obtained by comparing cesium and rubidium atomic fountain clocks [7]. Experiments have also been carried out comparing cesium and magnesium [8] and a H-maser compared with a Hg II clock [9]. There are many proposals for the search of the variation of α in atomic optical transitions, some of which were analyzed previously in [10–12]. In the present work we perform relativistic many-body calculations to find the relativistic energy shift for many two-valence-electron atoms and ions. Two-valence-electron atoms and ions were chosen since many new optical clocks experiments, some of which are currently under construction and some still under consideration, utilize these atoms and ions (e.g., Al II [13], Ca I [14], Sr I [15–17], In II [18–20], Yb I, and Hg I [21,22]).

II. THEORY

In the present work we perform calculations for closed-shell atoms and ions which can also be considered as atoms or ions with two valence electrons above closed shells. We start our calculations from the relativistic Hartree-Fock (RHF) (also known as the Dirac-Hartree-Fock) method in the V^N approximation. This means that RHF calculations are done for the ground state of the corresponding atom or ion with all electrons included in the self-consistent field. The use of the V^N RHF approximation ensures good convergence of the consequent configuration interaction (CI) calculations for the ground state. Good accuracy for excited states is achieved by using a large set of single-electron states. Note that there is an alternative approach which uses the V^{N-2} starting approximation (with two valence electrons removed from the RHF calculations). This approach has some advantages: it is simpler, and ground and excited states are treated equally. However, the convergence with respect to the size of the basis is not as good and the final results are better in the V^N approximation. We use the V^{N-2} approximation as a test of the accuracy of calculations of the relativistic energy shifts, while presenting all results in the V^N approximation.

We use a form of the single-electron wave function that explicitly includes a dependence on α:

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

This leads to the following form of the RHF equations (in atomic units):

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

$$g_n'(r) + \frac{\kappa_n}{r} g_n(r) + (\epsilon_n - \hat{V}_{HF}) f_n(r) = 0, \tag{2}$$

where $\kappa = (-1)^{l+j+1/2}(j+1/2)$, n is the principle quantum number, and $\hat{V}_{HF}$ is the Hartree-Fock potential. The nonrelativistic limit corresponds to setting $\alpha = 0$.

We then use the combination of the CI method with the many-body perturbation theory (MBPT) [23,24]. Interactions between valence electrons are treated using the CI method while correlations between the valence electrons and the core

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TABLE I. Energies of the *nsnp* configuration of two-electron atoms calculated using H^{CI}, $H^{CI}+\hat{\Sigma}_1$, and $H^{CI}+\hat{\Sigma}_1+\hat{\Sigma}_2$; comparison with experiment (cm^{-1})

Atom or ion	State	Experiment [30]	Theory		
			$\hat{H}^{CI}$	$\hat{H}^{CI}+\hat{\Sigma}_1$	$\hat{H}^{CI}+\hat{\Sigma}_{1,2}$
Al II	$^3P_0$	37393	36403	36987	37328
	$^3P_1$	37454	36466	37053	37393
	$^3P_2$	37578	36592	37185	37524
$^1P_1$	59852	59794	60647	60090	
Ca I	$^3P_0$	15158	13701	14823	15011
	$^3P_1$	15210	13750	14881	15066
	$^3P_2$	15316	13851	14997	15179
	$^1P_1$	23652	23212	24968	24378
Sr$_1$	$^3P_0$	14318	12489	13897	14169
	$^3P_1$	14504	12661	14107	14367
	$^3P_2$	14899	13021	14545	14786
	$^1P_1$	21698	20833	23012	22305
In II	$^3P_0$	42276	37825	39238	42304
	$^3P_1$	43349	38867	40394	43383
	$^3P_2$	45827	41168	42974	45904
	$^1P_1$	63034	62181	64930	62325
Yb I	$^3P_0$	17288	14377	16352	16950
	$^3P_1$	17992	15039	17189	17705
	$^3P_2$	19710	16550	19137	19553
	$^1P_1$	25068	24231	27413	26654
Hg I	$^3P_0$	37645	31864	32692	37420
	$^3P_1$	39412	33751	34778	39299
	$^3P_2$	44043	38155	39781	44158
	$^1P_1$	54069	50247	52994	56219
Tl II	$^3P_0$	49451	43831	43911	49865
	$^3P_1$	52393	47091	47350	52687
	$^3P_2$	61725	55988	56891	62263
	$^1P_1$	75660	74291	76049	74717

electrons are included by means of the MBPT. We can write the effective CI Hamiltonian for two valence electrons as

$$\hat{H}^{CI} = \hat{h}_1 + \hat{h}_2 + \hat{h}_{12}. \tag{3}$$

Here $\hat{h}_i$ ($i=1$ or 2) is an effective single-electron Hamiltonian given by

$$h_i = c\boldsymbol{\alpha}\times\mathbf{p} + (\beta-1)mc^2 - \frac{Ze^2}{r_i} + \hat{V}_{core} + \hat{\Sigma}_1, \tag{4}$$

and $\hat{V}_{core}$ is the Hartree-Fock potential created by the core electrons; it differs from $\hat{V}_{HF}$ in Eq. (2) by the contribution of the valence electrons. $\hat{\Sigma}_1$ is the one-electron operator that describes the correlation interaction between a valence electron and the core. The third term in Eq. (3) describes the interaction of the valence electrons with each other and can be written as

$$\hat{h}_{12} = \frac{e^2}{r_{12}} + \hat{\Sigma}_2, \tag{5}$$

where $\hat{\Sigma}_2$ is a two-particle operator that describes the effects of screening of the Coulomb interaction between the valence electrons by the core electrons. The operators $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ are calculated using the second order of MBPT.

We use the same set of single-electron basis states to construct two-electron wave functions for the CI calculations and to calculate $\hat{\Sigma}$. The set is based on the *B*-spline technique developed by Johnson *et al.* [25–27]. We use 40 *B* splines in a cavity of radius $R=40a_B$ (a_B is Bohr radius). The single-electron basis functions are linear combinations of 40 *B* splines and are also eigenstates of the Hartree-Fock Hamiltonian (in the V^N potential). Therefore, we have 40 basis functions in each partial wave including the *B*-spline approximations to the atomic core states. We use a different number of basis states for the CI wave functions and for the calculations of $\hat{\Sigma}$. Saturation comes much faster for the CI calculations. In these calculations we use 14 states above the core in each partial wave up to $l_{\max}=3$. Inclusion of states of higher principal quantum number or angular momentum does not change the result. To calculate $\hat{\Sigma}$ we use 30 out of 40 states in each partial wave up to $l_{\max}=4$.

The results for the energies are presented in Table I. We present the energies of the *nsnp* configuration of two-electron atoms or ions with respect to their ground state $^1S_0\ ns^2$. The states considered for atomic clock experiments are $^3P_0$ and $^3P_1$. However, we present the result for other states as well for completeness; these also make it easier to analyze the accuracy of the calculations. Also, transitions associated with some of these states are observed in quasar absorption spectra (e.g., the $^1S_0$-$^1P_1$ transition in Ca).

To demonstrate the importance of the core-valence correlations we include results of pure CI calculations (with no $\hat{\Sigma}$) as well as the results in which only $\hat{\Sigma}_1$ is included but $\hat{\Sigma}_2$ is not. One can see that the accuracy of pure CI calculations is about 10% while inclusion of core-valence correlations improves it significantly to the level of about 1%. The deviation from experiment of the final theoretical energies for the triplet states of all atoms except Yb is not more than 1%. For Yb it is 2%. The accuracy of the singlet states is about 1% for the ions, 3%–4% for Ca I, Sr I, and Hg I and 6% for Yb I. The accuracy of the fine-structure intervals ranges from 2% to 7%. The accuracy of calculations for Yb is not as good as for other atoms because the two-electron approximation is a poor approximation for this atom. Electrons from the $4f$ subshell, which are kept frozen in the present calculations, are relatively easy to excite and corresponding configurations give a substantial contribution to the energy. Note that we do include these excitations perturbatively in the $\hat{\Sigma}$ operator. However, due to their large contribution, the second-order treatment of the excitations from the $4f$ subshell is not very accurate. On the other hand, the CI+MBPT results for Yb are still much better than pure CI values.

Note also that the CI+MBPT results presented in Table I are in good agreement with similar calculations in Refs. [28,29].

TABLE II. Calculated q coefficients, for transitions from the ground state, using H^{CI}, $H^{CI}+\hat{\Sigma}_1$, and $H^{CI}+\hat{\Sigma}_1+\hat{\Sigma}_2$.

Atom or ion	State	$\hat{H}^{CI}$	$\hat{H}^{CI}+\hat{\Sigma}_1$	$H^{CI}+\hat{\Sigma}_{1,2}$	Other
Al II	$^3P_0$	138	142	146	
	$^3P_1$	200	207	211	
	$^3P_2$	325	340	343	
	$^1P_1$	266	276	278	
Ca I	$^3P_0$	108	115	125	
	$^3P_1$	158	173	180	230 [10]
	$^3P_2$	260	291	294	
	$^1P_1$	228	238	250	300 [10]
Sr I	$^3P_0$	384	396	443	
	$^3P_1$	560	609	642	667 [31]
	$^3P_2$	939	1072	1084	
	$^1P_1$	834	865	924	1058 [31]
In II	$^3P_0$	3230	2932	3787	4414 [12]
	$^3P_1$	4325	4125	4860	5323 [12]
	$^3P_2$	6976	7066	7767	7801 [12]
	$^1P_1$	6147	6103	6467	
Yb I	$^3P_0$	2339	2299	2714	
	$^3P_1$	3076	3238	3527	
	$^3P_2$	4935	5707	5883	
	$^1P_1$	4176	4674	4951	
Hg I	$^3P_0$	13231	9513	15299	
	$^3P_1$	15922	12167	17584	
	$^3P_2$	22994	19515	24908	
	$^1P_1$	20536	16622	22789	
Tl II	$^3P_0$	14535	11101	16267	19745 [12]
	$^3P_1$	18476	14955	18845	23213 [12]
	$^3P_2$	32287	28903	33268	31645 [12]
	$^1P_1$	28681	25160	29418	

TABLE III. Experimental energies and calculated q-coefficients (cm^{-1}) for transitions from the ground state ns^2 to the $nsnp$ configurations of two-electron atoms or ions.

Atom or ion	Z	State		Energy [30]	q
Al II	13	$3s3p$	$^3P_0$	37393.03	146
		$3s3p$	$^3P_1$	37453.91	211
		$3s3p$	$^3P_2$	37577.79	343
		$3s3p$	$^1P_1$	59852.02	278
Ca I	20	$4s4p$	$^3P_0$	15157.90	125
		$4s4p$	$^3P_1$	15210.06	180
		$4s4p$	$^3P_2$	15315.94	294
		$4s4p$	$^1P_1$	23652.30	250
Sr I	38	$5s5p$	$^3P_0$	14317.52	443
		$5s5p$	$^3P_1$	14504.35	642
		$5s5p$	$^3P_2$	14898.56	1084
		$5s5p$	$^1P_1$	21698.48	924
In II	49	$5s5p$	$^3P_0$	42275	3787
		$5s5p$	$^3P_1$	43349	4860
		$5s5p$	$^3P_2$	45827	7767
		$5s5p$	$^1P_1$	63033.81	6467
Yb I	70	$6s6p$	$^3P_0$	17288.44	2714
		$6s6p$	$^3P_1$	17992.01	3527
		$6s6p$	$^3P_2$	19710.39	5883
		$6s6p$	$^1P_1$	25068.22	4951
Hg I	80	$6s6p$	$^3P_0$	37645.08	15299
		$6s6p$	$^3P_1$	39412.30	17584
		$6s6p$	$^3P_2$	44042.98	24908
		$6s6p$	$^1P_1$	54068.78	22789
Tl II	81	$6s6p$	$^3P_0$	49451	16267
		$6s6p$	$^3P_1$	53393	18845
		$6s6p$	$^3P_2$	61725	33268
		$6s6p$	$^1P_1$	75600	29418

III. RESULTS AND DISCUSSION

In the vicinity of the α_0, the present-day value of α, the frequency of a transition, ω, can be written as

$$\omega = \omega_0 + qx, \tag{6}$$

where $x=(\alpha/\alpha_0)^2-1$, ω_0 is the present-day experimental value of the frequency, and the q coefficient is the relativistic energy shift that determines the frequency dependence on α. It is clear from the above expression that q coefficients can be described by

$$q = \left.\frac{d\omega}{dx}\right|_{x=0}.$$

Thus, in order to calculate q coefficients the atomic energy levels of the atoms and ions of interest at different values of x need to be calculated. The relativistic energy shift q is then calculated using the formulas

$$q = \frac{\omega(\Delta x) - \omega(-\Delta x)}{2\Delta x} \tag{7}$$

and

$$q = \frac{16[\omega(\Delta x) - \omega(-\Delta x)] - 2[\omega(2\Delta x) - \omega(-2\Delta x)]}{24\Delta x}. \tag{8}$$

The second formula is needed to check for nonlinear contributions to $d\omega/dx$. We use $\Delta x=0.1$ and $\Delta x=0.125$. The results are presented in Table II.

As for the energies, we use three different approximations to calculate relativistic energy shifts: (1) a pure CI approximation for two valence electrons, (2) a CI with $\hat{\Sigma}_1$, and (3) a CI+MBPT approximation with both $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ included. Inclusion of core-valence correlations leads to increased values of the q coefficients. This is because the correlation interaction of a valence electron with the core introduces an additional attraction which increase the density of the valence electron in the vicinity of the nucleus and thus emphasize the importance of the relativistic effects.

Note that $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ are of the same order and need to be included simultaneously to obtain reliable results. Σ_1 is much easier to calculate and inclusion of $\hat{\Sigma}_1$ alone often leads to significant improvements of the results for the energies (see Table I). However, the results for the q coefficients show that neglecting $\hat{\Sigma}_2$ may lead to significant loss in accuracy. Indeed, the results for q's with $\hat{\Sigma}_1$ alone are often smaller than those obtained in pure CI and CI+MBPT approximations and differ from final values by up to 50%. Since neglecting $\hat{\Sigma}_2$ cannot be justified, we present results without $\hat{\Sigma}_2$ for illustration purposes only.

The accuracy of the calculation of the q coefficients can be estimated by comparing the CI and CI+MBPT results calculated in the V^N and V^{N-2} approximations and also by comparing the final results for the energies (including fine-structure intervals) with experimental values. As one can see from Table II inclusion of the core-valence correlations can change the values of the q coefficients by more than 15%. However, the accuracy of the energies improves significantly when core-valence correlations are included. It is natural to expect that the final accuracy for the q coefficients is also higher when core-valence correlations are included. Comparison with our previous results also shows some deviation on approximately the same level (the largest relative discrepancy is for Ca where relativistic effects are small and high accuracy is not needed). Most of this discrepancy can be attributed to the inaccuracy of our old, less complete calculations. Comparison between the energies calculated in the V^N and V^{N-2} approximations and the experimental values suggests that 10% is a reasonable estimate of the accuracy of the present calculations of the relativistic energy shifts for Al II, Ca I, and Sr I, 15%for In II, 25% for Yb I, and 20% for Hg I and Tl II.

In Table III we present final values of the relativistic energy shifts together with the experimental energies.

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