Relativistic effects in two valence electron atoms and ions and 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 $\alpha$ 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, 2, 3]). Recent analysis of quasar absorption spectra suggests that the fine structure constant $\alpha$ might vary in space-time [4, 5, 6]. There is an intensive search for alternative ways to test whether $\alpha$ is varying. One of the very promising methods to study 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 $\alpha$ 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 changes with time. To relate a measurement of the change between two frequencies to a change in $\alpha$, the relativistic energy shifts are needed. The relativistic energy shift describes how a level moves as $\alpha$ 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 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 variation of $\alpha$ in atomic optical transitions, some of which were analyzed previously in [10, 11, 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, 16, 17], In II [18, 19, 20], Yb I, 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/ions with two valence electrons above closed shells. We start our calculations from the relativistic Hartree-Fock (RHF) (also known as Dirac-Hartree-Fock) method in the $V^N$ approximation. This means that RHF calculations are done for the ground state of the corresponding atom/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 $\alpha$:

$$\psi(r)_{\alpha jlm} = \frac{1}{r} \left( f(r)_{\alpha jlm}(r) \right) \frac{1}{i \alpha g(r)_{\alpha jlm}(r)} \right). \quad (1)$$

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

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

$$g_n'(r) + \frac{\kappa_n}{r} g_n(r) + (\epsilon_n - \hat{V}_{HF}) f_n(r) = 0, \quad (2)$$
where \( \kappa = (-1)^{l+j+1/2}(j + 1/2) \), \( n \) is the principle quantum number and \( V_{HF} \) is the Hartree-Fock potential. The non-relativistic limit corresponds to setting \( \alpha = 0 \).

We then use the combination of the configuration interaction (CI) method with the many-body perturbation theory (MBPT)\(^{22}\)\(^{23}\)\(^{24}\). Interactions between valence electrons are treated using the CI method while correlations between the valence electrons and the core electrons are included by means of the MBPT. We can write the effective CI Hamiltonian for two valence electrons as:

\[
\hat{H}^{CI} = \hat{h}_1 + \hat{h}_2 + \hat{h}_{12}
\]

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

\[
\hat{h}_i = c \alpha \times \mathbf{p} + (\beta - 1)mc^2 - \frac{Ze^2}{r_i} + \hat{V}_{\text{core}} + \hat{\Sigma}_1,
\]

\( \hat{V}_{\text{core}} \) is the Hartree-Fock potential created by the core electrons, it differs from \( V_{HF} \) 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

\[
\hat{h}_{12} = \frac{e^2}{r_{12}} + \hat{\Sigma}_2
\]

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 \( \Sigma \). The set is based on the B-spline technique developed by Johnson \textit{et al} \(^{25}\)\(^{26}\)\(^{27}\). 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 \( \Sigma \). 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 \( \Sigma \) 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/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 \( \Sigma \)) as well as the results in which only \( \hat{\Sigma}_1 \) and \( \hat{\Sigma}_2 \) are included by means of the MBPT.

| Atom/ State | Experiment | Theory |
|-------------|-------------|--------|
| AlII \(^3P_0 \) | 37393 | 36403 | 36987 |
| AlII \(^3P_1 \) | 37454 | 36466 | 37053 |
| AlII \(^3P_2 \) | 37578 | 36592 | 37185 |
| AlII \(^1P_1 \) | 59852 | 59794 | 60647 |
| Cal \(^3P_0 \) | 15158 | 13701 | 14823 |
| Cal \(^3P_1 \) | 15210 | 13750 | 14881 |
| Cal \(^3P_2 \) | 15316 | 13851 | 14997 |
| Cal \(^1P_1 \) | 23652 | 23212 | 24968 |
| SrI \(^3P_0 \) | 14318 | 12489 | 13897 |
| SrI \(^3P_1 \) | 14504 | 12661 | 14107 |
| SrI \(^3P_2 \) | 14899 | 13021 | 14545 |
| SrI \(^1P_1 \) | 21698 | 20833 | 23012 |
| InII \(^3P_0 \) | 42276 | 37825 | 39238 |
| InII \(^3P_1 \) | 43349 | 38867 | 40394 |
| InII \(^3P_2 \) | 45827 | 41168 | 42974 |
| InII \(^1P_1 \) | 63034 | 62181 | 64930 |
| Ybl \(^3P_0 \) | 17288 | 14377 | 16352 |
| Ybl \(^3P_1 \) | 17902 | 15039 | 17189 |
| Ybl \(^3P_2 \) | 19710 | 16550 | 19137 |
| Ybl \(^1P_1 \) | 25068 | 24231 | 27413 |
| Hgl \(^3P_0 \) | 37645 | 31864 | 32692 |
| Hgl \(^3P_1 \) | 39412 | 33751 | 34778 |
| Hgl \(^3P_2 \) | 44043 | 38155 | 39781 |
| Hgl \(^1P_1 \) | 54069 | 50247 | 52994 |
| TII \(^3P_0 \) | 49451 | 43831 | 44911 |
| TII \(^3P_1 \) | 52393 | 47091 | 47350 |
| TII \(^3P_2 \) | 61725 | 55988 | 56891 |
| TII \(^1P_1 \) | 75660 | 74291 | 76049 |

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\(^{-1} \)).
TABLE II: Calculated $q$ coefficients, for transitions from the ground state, using $H^{CI}$, $H^{CI} + \Sigma_1$ and $H^{CI} + \Sigma_1 + \Sigma_2$ coefficients can be described by

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

where $x = (\frac{s}{\omega})^2 - 1$, $\omega_0$ is the present day experimental value of the frequency and the $q$ coefficient is the relativistic energy shift that determines the frequency dependence on $\alpha$. It is clear from the above expression that $q$ coefficients can be described by

$$q = \frac{d\omega}{dx}_{x=0}$$

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 formulae

$$q = \frac{\Delta (\omega_0 - \omega)}{2\Delta x}$$

and

$$q = \frac{16(\omega_0 \Delta x - \omega(-\Delta x) - 2(\omega(2\Delta x) - \omega(-2\Delta x)))}{24\Delta x}$$

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

As for the energies, we use three different approximations to calculate relativistic energy shifts: (1) pure CI approximation for two valence electrons, (2) CI with $\Sigma_1$ and (3) CI+MBPT approximation with both $\Sigma_1$ and $\Sigma_2$ included. Inclusion of core-valence correlations lead 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. $\hat{\Sigma}_1$ 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 purpose 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 suggest 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.

Acknowledgments

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