Improved calculation of relativistic shift and isotope shift in Mg I

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We present an ab initio method of calculation of isotope shift and relativistic shift in atoms with a few valence electrons. It is based on an energy calculation involving combination of the configuration interaction method and many-body perturbation theory. This work is motivated by analyses of quasar absorption spectra that suggest that the fine structure constant $\alpha$ was smaller at an early epoch. Relativistic shifts are needed to measure this variation of $\alpha$, while isotope shifts are needed to resolve systematic effects in this study. The isotope shifts can also be used to measure isotopic abundances in gas clouds in the early universe, which are needed to study nuclear reactions in stars and supernovae and test models of chemical evolution. This paper shows that isotope shift in magnesium can be calculated to very high precision using our new method.

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I. INTRODUCTION

The motivation for this work comes from recent studies of quasar absorption spectra designed to probe $\alpha$ in the distant past. Atomic transition frequencies depend on $\alpha$, and by comparing frequencies on Earth with those in quasar absorption spectra, one can deduce whether or not $\alpha$ was different in the early universe. While some studies have revealed a significant deviation from zero (Refs. [1, 2, 3, 4]), other groups using a different telescope have not (Refs. [5, 6, 7, 8]).

One of the possible major sources of systematic effects in these studies is that the isotopic abundance ratios in gas clouds in the early universe could be very different to those on Earth. A “conspiracy” of several isotopic abundances may provide an alternative explanation for the observed variation in spectra [9, 10, 11, 12]. In order to test this possibility it is necessary to have accurate values for the isotope shift (IS) for the relevant atomic transitions [10, 11]. Experimental data are available for very few of them; therefore, accurate calculations are needed in order to make the most comprehensive analysis possible.

The need for accurate isotope shifts is further motivated by a wish to study isotopic evolution in the universe. The isotopic abundances of gas clouds may be measured independently of a variation in $\alpha$ [10]. This is important for testing models of nuclear reactions in stars and supernovae and of the chemical evolution of the universe.

Previously we have calculated isotope shift in atoms with one valence electron using many-body perturbation theory (MBPT) [11], and for neutral magnesium using the configuration interaction (CI) method [12]. Both of these papers used the finite-field scaling method for the perturbation. In a sense our method combines these two methods by including core-valence correlations into our CI method using MBPT. Magnesium is one of the simplest and well studied two-valence-electron atoms. Because of that it is often used as a test ground for different methods of atomic calculations. In this paper we show that we can calculate the isotope shift of some magnesium transitions for which experimental values are available.

II. METHOD

The isotope shifts of atomic transition frequencies come from two sources: the finite size of the nuclear charge distribution (the “volume” or “field” shift), and the finite mass of the nucleus (see, e.g. [13]). The energy shift due to recoil of the nucleus is $(1/2M)p_N^2 = (1/2M)(\Sigma p_i)^2$. Furthermore this “mass shift” is traditionally divided into the normal mass shift (NMS) and the specific mass shift (SMS). The normal mass shift is given by the operator $(1/2M)\Sigma p_i^2$, which is easily calculated from the transition frequency. The SMS operator is $(1/M)\Sigma_{i<j}(p_i \cdot p_j)$ which is difficult to evaluate accurately.

The shift in energy of any transition in an isotope with mass number $A'$ with respect to an isotope with mass number $A$ can be expressed as

$$\delta \nu^{A',A} = \left( k_{\text{NMS}} + k_{\text{SMS}} \right) \left( \frac{1}{A'} - \frac{1}{A} \right) + F \delta \langle r^2 \rangle^{A',A}, \quad (1)$$

where the normal mass shift constant is

$$k_{\text{NMS}} = -\frac{\nu}{1823}, \quad (2)$$

and $\langle r^2 \rangle$ is the mean square nuclear radius. The value 1823 refers to the ratio of the atomic mass unit to the electron mass.

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In this paper we develop a method for calculating the specific mass shift $k_{\text{SMS}}$ for atoms with several valence electrons. It is worth noting that in this paper we use the convention $\delta \nu^{A',A} = \nu^{A'} - \nu^A$.

Following our previous work, we are looking for an “all orders” method of calculation. Again we have found that the finite-field scaling method is very useful in this respect. The rescaled SMS operator is added to the many-particle Hamiltonian

$$H_\lambda = H_0 + \lambda H_{\text{SMS}} = H_0 + \lambda \sum_{i<j} p_i \cdot p_j.$$  \hspace{1cm} (3)

The eigenvalue problem for the new Hamiltonian is solved for various $\lambda$, and then we recover the specific mass shift constant as

$$k_{\text{SMS}} = \lim_{\lambda \to 0} \frac{dE}{d\lambda}.$$  \hspace{1cm} (4)

The operator $\mathbf{\lambda}$ has the same symmetry and structure as the initial Hamiltonian $H_0$ (see the Appendix, Ref. [11]).

We have also calculated the relativistic shift for transitions in magnesium using a similar method. These are needed in order to measure variation of $\alpha$ for various $\lambda$. For valence and core-valence effects, included using MBPT, make little difference to the $\Sigma_1$ only, and both $\Sigma_1$ and $\Sigma_2$. This is easily justified. The fact that in previous works for atoms with several valence electrons these have either been neglected entirely or included using a simple fitting procedure based on the polarisability of the core [11].

TABLE I: Energy of Mg I levels relative to the ground state ($3s^2 1S_0$).

| Level        | Experiment | CI | CI + $\Sigma_1$ | CI + $\Sigma_1$ + $\Sigma_2$ |
|--------------|-------------|----|-----------------|-----------------------------|
| 3s3p $^3P_0^0$ | 21850       | 20910 | 21676 | 21772       |
| 3s3p $^3P_1^0$ | 21870       | 20930 | 21698 | 21794       |
| 3s3p $^3P_2^0$ | 21911       | 20971 | 21742 | 21837       |
| 3s3p $^1P_1^0$ | 35051       | 34491 | 35474 | 35050       |
| 3s4s $^3S_1^0$ | 41197       | 40406 | 41469 | 41126       |
| 3s4s $^1S_0^0$ | 43503       | 42667 | 43744 | 43431       |
| 3s3d $^3D_2^0$ | 46403       | 45123 | 46475 | 46306       |
| 3s4p $^3P_0^0$ | 47841       | 46919 | 48079 | 47756       |
| 3s4p $^3P_1^0$ | 47844       | 46923 | 48082 | 47760       |
| 3s4p $^3P_2^0$ | 47851       | 46929 | 48090 | 47767       |
| 3s3d $^3D_3^0$ | 47957       | 46973 | 48227 | 47880       |
| 3s3d $^3D_2^0$ | 47957       | 46973 | 48227 | 47879       |
| 3s3d $^3D_1^0$ | 47957       | 46973 | 48227 | 47879       |
| 3s4p $^1P_1^0$ | 49347       | 48490 | 49672 | 49277       |
| 3s4d $^3D_2^0$ | 53135       | 52041 | 53337 | 53037       |
| 3s4d $^3D_1^0$ | 54192       | 53243 | 54486 | 54111       |
| 3p$^2$ $^3P_0^0$ | 57813       | 56182 | 58003 | 57706       |

III. CALCULATION AND RESULTS

The CI part of the calculation is very similar to the large basis set calculation in Ref. [12]. We first solved the Dirac-Fock equations for the core electrons; we use the $V^{-2}$ approximation, so the core includes the orbitals $1s_{1/2}, 2s_{1/2}, 2p_{1/2},$ and $2p_{3/2}$. For valence and virtual orbitals we used a basis formed by diagonalizing the Dirac-Fock operator on the basis set of B-splines and excluding orbitals with high energy (for a description of this method as applied in atomic physics, see, e.g., Refs. [10, 21, 21]).

The full two-electron CI uses the basis $17spdf$, which includes the orbitals $1-17s_{1/2}, 2-17p_{j}, 3-17d_{j},$ and $4-17f_{j}$. It is very close to the saturation of the valence CI. The MBPT basis can be larger, since the calculation merely involves a summation over the virtual orbitals; we have therefore used the basis $32spdf$ for this part of the calculation, which is essentially complete.

Table II shows that our ab initio calculation of the spectrum is within 0.4% of the experimental spectrum for all considered levels. The relativistic shifts ($q$-values) are presented in Table III. Table III presents the resulting SMS level shift constants, $k_{\text{SMS}}$ of Eq. (4). In each table we present results of the pure CI calculation (which agree with our previous calculation Ref. [12]), as well as calculations including $\Sigma_1$ only, and both $\Sigma_1$ and $\Sigma_2$.

It is worth noting a few points. Firstly, the core-valence effects, included using MBPT, make little difference to the $q$-values (less than 10%). This again justifies the fact that in previous works for atoms with several valence electrons these have either been neglected entirely or included using a simple fitting procedure based on the polarisability of the core [12].

The core-valence effects are much more important for the SMS calculation. In particular the single-valence-electron diagrams (included in $\Sigma_1$) can improve accuracy drastically in cases where the pure CI method is not very good. Although $\Sigma_2$ is important for energy calculation, it appears to make little difference to $k_{\text{SMS}}$. This is easily understood since the most important two-body diagram (the direct diagram, corresponding to the screening of the...
TABLE II: Relativistic shift of Mg I transitions relative to the ground state (3s2 1S0).

| Upper Level | Energy | 3s3p J = 3/2 | 3s3p J = 1/2 | 3s4s J = 1/2 | 3s4d J = 3/2 | 3s4d J = 1/2 | 3p2 J = 1/2 |
|-------------|--------|-------------|-------------|-------------|-------------|-------------|-------------|
| 53888 3/2   | 61     | 66          | 68          |             |             |             |             |
| 53885 1/2   | 81     | 88          | 89          |             |             |             |             |
| 53872 3/2   | 21911  | 122         | 132         |             |             |             |             |
| 53869 1/2   | 35051  | 86          | 94          |             |             |             |             |
| 53866 3/2   | 43503  | 60          | 65          | 66          |             |             |             |
| 53863 1/2   | 46403  | 117         | 123         | 122         |             |             |             |
| 53860 3/2   | 47841  | 67          | 73          | 73          |             |             |             |
| 53857 1/2   | 47844  | 70          | 76          | 77          |             |             |             |
| 53854 3/2   | 47851  | 77          | 83          | 84          |             |             |             |
| 53851 1/2   | 47957  | 79          | 85          | 86          |             |             |             |
| 53848 3/2   | 47957  | 79          | 85          | 86          |             |             |             |
| 53845 1/2   | 47957  | 79          | 85          | 86          |             |             |             |
| 53842 3/2   | 49347  | 80          | 86          | 87          |             |             |             |
| 53839 1/2   | 53135  | 94          | 101         | 102         |             |             |             |
| 53836 3/2   | 54192  | 73          | 79          | 80          |             |             |             |
| 53833 1/2   | 57813  | 198         | 214         | 214         |             |             |             |

TABLE III: Calculations of the specific mass shift constants kSMS for Mg I transitions to the ground state (in GHzamu).

| Upper Level | Energy | kSMS (GHzamu) |
|-------------|--------|---------------|
| 3s3p J = 3/2 | 21850  | -378          |
| 3s3p J = 1/2 | 21870  | -377          |
| 3s3p J = 3/2 | 21911  | -375          |
| 3s3p J = 1/2 | 35051  | 231           |
| 3s4s J = 1/2 | 41197  | 43            |
| 3s4s J = 1/2 | 43503  | 13            |
| 3s3d J = 3/2 | 46403  | -345          |
| 3s3d J = 1/2 | 47841  | -17           |
| 3s3d J = 1/2 | 47844  | -16           |
| 3s3d J = 1/2 | 47851  | -16           |
| 3s3d J = 1/2 | 47957  | 52            |
| 3s3d J = 1/2 | 47957  | 52            |
| 3s3d J = 1/2 | 47957  | 52            |
| 3s3d J = 1/2 | 49347  | 5             |
| 3s3d J = 1/2 | 53135  | 100           |
| 3s3d J = 1/2 | 54192  | 32            |
| 3p2 J = 1/2  | 57813  | -225          |

IV. CONCLUSION

We have presented a method for the calculation of the isotope-shift in many-electron atoms. It is based on the finite-field method, with an energy calculation that combines CI for the valence electrons and MBPT for the core-valence correlations. We have tested the method in magnesium, and the agreement was found to be very good for all transitions. In particular, for the purposes of resolving systematic errors in the search for α-variation, and for studies of isotopic evolution of the universe, such accuracy is high enough.

We have also used the method to generate more precise values for the relativistic shift (q-values). These were found to be within 10% of those found using previous methods, as expected.

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TABLE IV: Comparison of our calculated SMS with that extracted from experiment for several transitions (in MHz). The isotope shifts are between $^{24}$Mg and $^{25}$Mg. Also presented are the results of Refs. [22] and [23] for theoretical comparison. We have neglected the field shift; it is of the order of 20-30 MHz.

| Transition | $\lambda$ (Å) | IS(expt.) | NMS | SMS |
|------------|---------------|------------|-----|-----|
| $3s^2 \, 1S_0 \rightarrow 3s3p \, 1P^o_1$ | 4572 | 2683(0)$^b$ | 1153 | 1208 | 1559 | 1573 | 1530 | 1378 | 1666 |
| $3s^2 \, 1S_0 \rightarrow 3s3p \, 1P^o_1$ | 2853 | 1412(21)$^b$ | 1848 | -740 | -383 | -428 | -436 | -409 |
| $3s^2 \, 1S_0 \rightarrow 3s3p \, 1P^o_1$ | 1300(31)$^c$ | -458 |
| $3s3p \, 3P^o_0 \rightarrow 3s4s \, 3S^o_1$ | 5169 | -306(6)$^d$ | 1020 | -1347 | -1371 | -1419 | -1416 |
| $3s3p \, 3P^o_1 \rightarrow 3s4s \, 3S^o_1$ | 5174 | -300(5)$^d$ | 1019 | -1345 | -1369 | -1416 | -1409 |
| $3s3p \, 3P^o_2 \rightarrow 3s4s \, 3S^o_1$ | 5185 | -300(7)$^d$ | 1017 | -1339 | -1363 | -1411 | -1407 |
| $3s3p \, 3P^o_2 \rightarrow 3p^2 \, 3P^o_0$ | 2782 | 1810(80)$^e$ | 1895 | -486 | -56 | -86 | -85 |
| $3s3p \, 3P^o_0 \rightarrow 3s3d \, 3D^o_1$ | 3830 | 60(15)$^b$ | 1376 | -1377 | -1283 | -1329 | -1316 | -1269 |
| $3s3p \, 3P^o_2 \rightarrow 3s3d \, 3D^o_{1,2}$ | 3833 | 61(3)$^b$ | 1375 | -1374 | -1280 | -1326 | -1314 |
| $3s3p \, 3P^o_2 \rightarrow 3s3d \, 3D^o_{1,2,3}$ | 3839 | 58(4)$^b$ | 1373 | -1368 | -1274 | -1321 | -1315 |
| $3s3p \, 3P^o_1 \rightarrow 3s4d \, 3D^o_1$ | 3004 | 420(20)$^e$ | 1704 | -1309 | -1241 | -1291 | -1284 |
| $3s3p \, 3P^o_1 \rightarrow 3s4d \, 3D^o_2$ | 5530 | 2107(15)$^d$ | 953 | 1059 | 1173 | 1195 | 1154 |

$^a$Stern et al., 1993  $^b$Hallstadius, 1979  $^c$Le Boiteux et al., 1998  $^d$Hallstadius and Hansen, 1978  $^e$Novero et al., 1992  $^f$M. T. Murphy, V. V. Flambaum, A. Dzuba, J. D. Barrow, C. W. Churchill, J. X. Prochaska, and A. M. Wolfe, Phys. Rev. Lett. 87, 091301 (2001).
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