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Configuration-interaction calculation for the isotope shift in Mg I

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We present an *ab initio* method of calculation of isotope shift in atoms with a few valence electrons, based on the configuration-interaction calculation of energy. The main motivation for developing the method comes from the need to analyze whether differences in isotope abundance in early universe can contribute to the observed anomalies in quasar absorption spectra. The current best explanation for these anomalies is the assumption that the fine structure constant α was smaller at early epoch. We show that we can calculate the isotope shift in magnesium with good accuracy.

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I. INTRODUCTION

The motivation for this work comes from recent studies of quasar absorption spectra that reveal a possible change in α since the early universe [1]. 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 [2]. In order to test this possibility it is necessary to have accurate values for the isotope shift (IS) for the relevant atomic transitions. Experimental data are available for only very few of them; therefore, accurate calculations are needed to make the most comprehensive analysis possible.

Previously we have calculated isotope shift in atoms with one valence electron [3]. This work represents an important step in developing a method for the calculation of isotope shift in atoms with more than one valence electron. The method used here is similar to our previous calculations of the α dependence of transition frequencies for ions with several valence electrons [4]. It includes Dirac-Fock calculation of the core and configuration interaction (CI) for the valence electrons in combination with the finite-field method for the perturbation. Magnesium is one of the simplest and well studied two-electron atoms. Because of that it is often used as a test ground for different methods of atomic calculations. In this Brief Report 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., Ref. [5]). The energy shift due to recoil of the nucleus is $(1/2M)\boldsymbol{p}_N^2=(1/2M)(\Sigma \boldsymbol{p}_i)^2$. 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 $(1/2M)\Sigma \boldsymbol{p}_i^2$, which is easily calculated from the transition frequency. The SMS operator is $(1/M)\Sigma_{i<j}(\boldsymbol{p}_i\cdot\boldsymbol{p}_j)$ 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

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

where the normal mass shift constant is

$$k_{\mathrm{NMS}}=-\frac{\nu}{1823} \qquad (2)$$

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.

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

Following our previous work on single valence electron atoms (Ref. [3]) we are looking for an "all order" method of calculation. Again we have found that the finite-field scaling

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*Electronic address: jcb@phys.unsw.edu.au method is very useful in this respect. The rescaled SMS operator is added to the many-particle Hamiltonian

$$H_\lambda = H_0 + \lambda H_{\text{SMS}} = H_0 + \lambda \sum_{i<j} \boldsymbol{p}_i \cdot \boldsymbol{p}_j . \tag{3}$$

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

$$k_{\text{SMS}} = \lim_{\lambda \to 0} \frac{dE}{d\lambda} . \tag{4}$$

The operator (3) has the same symmetry and structure as the initial Hamiltonian H_0 (see the Appendix, Ref. [3]).

In this work we restrict ourselves to the frozen-core approximation. We first solve the Dirac-Fock equations for the core and valence electrons. Then we generate a basis set that includes the core and valence orbitals, and a number of virtual orbitals. Finally we do the full configuration-interaction calculation.

The SMS operator for the valence electrons in the frozen-core approximation can be divided into the core, one-electron and two-electron parts:

$$H_{\text{SMS}} = H_{\text{SMS}}^{(0)} + H_{\text{SMS}}^{(1)} + H_{\text{SMS}}^{(2)} . \tag{5}$$

The first term in Eq. (5) corresponds to the change of the core potential. It accounts for the change of the core orbitals when the Dirac-Fock equations are solved for the operator H_λ. The term $H_{\text{SMS}}^{(1)}$ accounts for the exchange interaction of the valence electrons with the core:

$$\langle i | H_{\text{SMS}}^{(1)} | k \rangle = \sum_{j=1}^{N_{\text{core}}} \langle i,j | \boldsymbol{p}_1 \cdot \boldsymbol{p}_2 | j,k \rangle . \tag{6}$$

The last term corresponds to the specific mass shift between the two valence electrons, $\boldsymbol{p}_1 \cdot \boldsymbol{p}_2$.

III. CALCULATION AND RESULTS

We are using the Dirac-Fock code [6], which was modified for the Hamiltonian (3). The CI calculations are made with the help of the modification [7] of the code [8]. In order to study the role of the valence correlations we made three different calculations.

(1) The basic one-configurational calculation for the ground state ${}^1S_0[3s^2]$ and for the ${}^{1,3}P_J[3s3p]$ states. All core orbitals and orbitals $3s$ and $3p$ are formed in the V^{N-2} approximation (i.e., by solving Dirac-Fock equations for the core).

(2) Full two-electron CI for the medium size basis set $[8sp5d]$, which includes the orbitals $1-8s_{1/2}$, $2-8p_j$, and $3-5d_j$. The $3s$, $3p$, and $3d$ orbitals are solutions of the V^{N-2} Dirac-Fock potential. The remaining virtual orbitals are constructed by multiplying the previous orbital of the same partial wave by the simple radial function and orthogonalizing with the other orbitals [9].

(3) Full two-electron CI for the basis set $[12spd9f]$. This basis set is 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., Ref. [10]).

TABLE I. Calculations of the specific mass shift constants k_{SMS} for Mg I levels (in GHz amu). Individual contributions from Eq. (5) are presented, as well as the total. For some levels we give medium (M) CI and one-configurational results (S) in addition to the large (L) CI ones.

			k_{SMS}		
Level	(0)	(1)	(2)	Σ	CI
${}^1S_0(3s^2)$	559	−883	131	−193	L
${}^1S_0(3s^2)$	561	−881	135	−186	M
${}^1S_0(3s^2)$	857	−1125	0	−268	S
${}^3S_1(3s4s)$	422	−615	44	−149	L
${}^3S_1(3s4s)$	431	−624	52	−142	M
${}^1S_0(3s4s)$	415	−615	21	−179	L
${}^1S_0(3s4s)$	424	−630	30	−177	M
${}^1D_2(3s3d)$	343	−616	−267	−541	L
${}^3D_1(3s3d)$	375	−561	41	−144	L
${}^3D_1(3s3d)$	381	−571	−10	−200	M
${}^3D_2(3s3d)$	375	−561	41	−144	L
${}^3D_3(3s3d)$	375	−561	41	−144	L
${}^3P_0^o(3s3p)$	428	−853	−144	−570	L
${}^3P_1^o(3s3p)$	428	−852	−145	−569	L
${}^3P_2^o(3s3p)$	428	−850	−145	−567	L
${}^3P_2^o(3s3p)$	431	−850	−142	−561	M
${}^3P_2^o(3s3p)$	759	−1161	−266	−668	S
${}^1P_1^o(3s3p)$	408	−698	329	38	L
${}^1P_1^o(3s3p)$	411	−700	341	52	M
${}^1P_1^o(3s3p)$	946	−1163	265	49	S
${}^3P_0^o(3s4p)$	402	−630	13	−215	L
${}^3P_1^o(3s4p)$	402	−629	13	−215	L
${}^3P_2^o(3s4p)$	402	−629	13	−214	L

Below we refer to these calculations as small, medium, and large. The large calculation is already very close to the saturation of the valence CI. Here the difference between the theoretical spectrum and experiment is mostly caused by the neglect of the core-valence correlations. The latter were studied, for example, in Ref. [11]. For Mg I the typical corrections to the valence energies and transition frequencies were found to be of the order of a few percent.

Table I presents the resulting SMS level shift constants, k_{SMS} of Eq. (1), in different approximations. The contributions of individual terms in Eq. (5) are given, as well as their sum. It is interesting to note that all of the terms are large in comparison to the total SMS. There is a large cancellation between contributions within levels, and also between different levels. This shows that high accuracy is required in each term, so that the residual SMS in transitions is still correct after cancellation.

Comparison of the different approximations shows a strong dependence on the size of the basis sets. We see that it

TABLE II. Comparison with experiment of the SMS for several transitions (in MHz) between ^{26}Mg and ^{24}Mg. Also presented are the results of Ref. [12] for a theoretical comparison. We have assumed that the field shift is negligible.

Transition	λ Å	IS (expt.)	NMS	SMS Expt.	SMS Present	SMS Ref. [12]
$^1S_0(3s^2)\rightarrow {^3P_1^o}(3s3p)$	4572	2683(0)[a]	1153	1530	1205	1378
$^1S_0(3s^2)\rightarrow {^1P_1^o}(3s3p)$	2853	1412(21)[b]	1848	−436	−740	
$^1S_0(3s^2)\rightarrow {^1P_1^o}(3s3p)$		1390(31)[c]		−458		
$^3P_0^o(3s3p)\rightarrow {^3S_1}(3s4s)$	5169	−396(6)[d]	1020	−1416	−1349	
$^3P_1^o(3s3p)\rightarrow {^3S_1}(3s4s)$	5174	−390(5)[d]	1019	−1409	−1346	
$^3P_2^o(3s3p)\rightarrow {^3S_1}(3s4s)$	5185	−390(7)[d]	1017	−1407	−1340	
$^3P_1^o(3s3p)\rightarrow {^3P_0}(3p^2)$	2782	1810(80)[e]	1895	−85	−487	
$^3P_0^o(3s3p)\rightarrow {^3D_1}(3s3d)$	3830	60(15)[b]	1376	−1316	−1365	−1269
$^3P_1^o(3s3p)\rightarrow {^3D_{1,2}}(3s3d)$	3833	61(3)[b]	1375	−1314	−1362	
$^3P_2^o(3s3p)\rightarrow {^3D_{1,2,3}}(3s3d)$	3839	58(4)[b]	1373	−1315	−1356	
$^3P_1^o(3s3p)\rightarrow {^3D_1}(3s4d)$	3094	420(20)[e]	1704	−1284	−1375	
$^1P_1^o(3s3p)\rightarrow {^1D_2}(3s4d)$	5530	2107(15)[d]	953	1154	1224	

[a] Sterr *et al.* [14].
[b] Hallstadius [15].
[c] Le Boiteux *et al.* [16].
[d] Hallstadius and Hansen[17].
[e] Novero *et al.* [18].

is very important to saturate the basis as completely as possible. In some cases the SMS changes drastically even between the medium and the large basis sets. In particular, the difference between large and medium SMS calculation for the level $^3D_1(3s3d)$ is 39%. That is, mostly due to the f-wave contribution, which is absent in the medium basis set. Note that the SMS operator can only mix orbitals with $\Delta l=1$. That is why the f-wave contribution is more important for the levels of the configuration $3s3d$. On the other hand, for the same reason, the contribution of the higher partial waves to the considered levels is suppressed.

Analysis of Table I shows that valence correlations tend to decrease the contributions of the first two terms of the SMS operator. The third (two-particle) term of the SMS operator is generally not screened. On the contrary, for some levels the two-particle contribution grows with the size of the basis set. Note that the final value of the two-particle contribution to the ground state SMS is of the same order as the other contributions, as it is for most other states, while in the one-configurational approximation it is zero.

In Table II we compare the results of our calculation with experiment for SMS in transitions between ^{26}Mg and ^{24}Mg. Also presented for comparison are the results of Veseth (Ref. [12]). That paper used nonrelativistic many-body perturbation theory within the algebraic approximation to calculate the isotope shift to third order for some transitions.

We have also applied the finite-field scaling method to calculate the field shift in Mg. By following the definitions for field shift given in Ref. [3], and using the same approximations for the CI calculation, we found that it was less than 2% of the normal mass shift for all relevant transitions. The field shift is smaller than omissions in the mass shift calculation, notably the core-valence correlations; thus for simplicity we have neglected the field shift from our analysis in this Brief Report.

Core-valence correlations have been studied for the one-electron atoms in Refs. [3,13] and shown to be quite noticeable. They can explain the difference between our calculations and the experiment in Table II. Core-valence correlations are usually more important for the ground state than for excited states. That may be the reason why the largest discrepancy with the experiment is for the transitions from the ground state.

IV. CONCLUSION

We have presented a method for the calculation of the isotope shift in many-electron atoms using the CI for the valence electrons in combination with the finite-field method, and tested the method in magnesium. The agreement was found to be quite good for all transitions. Even for the transitions from the ground state $^1S_0$ to the $J=1$ levels of the configuration $3s3p$, where the error is largest, it constitutes about 20% of the total IS. In particular, for the purposes of resolving systematic errors in the search for α variation (Refs. [1,2]), such accuracy is high enough.

Further work on magnesium could include core correlations, using the extensions to CI outlined in Ref. [7]. We have decided not to do this, however, because we wanted a general method for calculating IS in many electron atoms. The method of including core-valence correlations in the valence CI with the help of the effective Hamiltonian has proven to be very effective for atoms with two or three valence electrons, but becomes less reliable for atoms with more than three valence electrons. Unfortunately, most of the ions of astrophysical interest have many electrons in the open shells. For such ions valence correlations are the most important ones and we plan to use this technique to calculate isotope shift for the transitions that were used to detect variation of α. That will provide stringent limits on the size of the systematic error due to variation in isotope abundance.

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