

Calculation of relativistic and isotope shifts in Mg I

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We present an *ab initio* method of calculation of the isotope and relativistic shifts in atoms with a few valence electrons. It is based on an energy calculation involving the 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 α was smaller at an early epoch. Relativistic shifts are needed to measure this variation of α , 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 the isotope shift in magnesium can be calculated to very high precision using our method.

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I. INTRODUCTION

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

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 from those on earth. A “conspiracy” of several isotopic abundances may provide an alternative explanation for the observed variation in spectra [8–10]. In order to test this possibility it is necessary to have accurate values for the isotope shift (IS) for the relevant atomic transitions [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 α [11]. 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) [12], and for neutral magnesium using the configuration-interaction (CI) method [13]. 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 best-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., [14]). The energy shift due to recoil of the nucleus is $(1/2M)\mathbf{p}_N^2 = (1/2M)(\sum \mathbf{p}_i)^2$. 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 $(1/2M)\sum \mathbf{p}_i^2$, which is easily calculated from the transition frequency. The SMS operator is $(1/M)\sum_{i<j}(\mathbf{p}_i \cdot \mathbf{p}_j)$ 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

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

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.

In this paper 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 paper we use the convention $\delta\nu^{A',A} = \nu^{A'} - \nu^A$.

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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

$$H_\lambda = H_0 + \lambda H_{\text{SMS}} = H_0 + \lambda \sum_{i < j} \mathbf{p}_i \cdot \mathbf{p}_j. \quad (3)$$

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

$$k_{\text{SMS}} = \lim_{\lambda \rightarrow 0} \frac{dE}{d\lambda}. \quad (4)$$

The operator (3) has the same symmetry and structure as the initial Hamiltonian H_0 (see the Appendix of Ref. [12]).

We have also calculated the relativistic shift for transitions in magnesium using a similar method. These are needed in order to measure variation of α [1–6]. The dependence of transition frequencies on α can be expressed as

$$\omega = \omega_0 + qx, \quad (5)$$

where $x = (\alpha/\alpha_0)^2 - 1$, α_0 is the laboratory value of the fine-structure constant, and ω and ω_0 are the frequencies of the transition in the absorption clouds and in the laboratory, respectively. We vary α directly in codes and hence calculate q . This method is described in detail in our earlier work (Refs. [15–17]).

To calculate the energy, we use a combination of configuration-interaction and many-body perturbation theory, as was done in Refs. [18,19]. We generate a basis set that includes the core and valence orbitals and a number of virtual orbitals. Then we do the full configuration-interaction calculation in the frozen-core approximation. Core-valence correlation effects are taken into account using a MBPT operator Σ , which is added to the CI Hamiltonian (for a full account of this procedure, see Ref. [18]). The MBPT operator is separated into two parts Σ_1 and Σ_2 , which include all one-valence-electron diagrams and two-valence-electron diagrams, respectively. The operators are calculated to second order, which was shown to be sufficient for single-valence-electron atoms when used with a finite-field method [12].

III. CALCULATION AND RESULTS

The CI part of the calculation is very similar to the large-basis-set calculation in Ref. [13]. We first solved the Dirac-Fock equations for the core electrons; we use the V^{N-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. [20–22]).

The full two-electron CI uses the basis $17spdf$, which includes the orbitals $(1-17)s_{1/2}$, $(2-17)p_j$, $(3-17)d_j$, and $(4-17)f_j$. It is very close to the saturation of the valence CI. The MBPT basis can be larger, since the calculation merely

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

Level	Experiment	Energy (cm ⁻¹)		
		CI	CI+ Σ_1	CI+ Σ_1 + Σ_2
$3s3p \ ^3P_0^o$	21 850	20 910	21 676	21 772
$3s3p \ ^3P_1^o$	21 870	20 930	21 698	21 794
$3s3p \ ^3P_2^o$	21 911	20 971	21 742	21 837
$3s3p \ ^1P_1^o$	35 051	34 491	35 474	35 050
$3s4s \ ^3S_1$	41 197	40 406	41 469	41 126
$3s4s \ ^1S_0$	43 503	42 667	43 744	43 431
$3s3d \ ^1D_2$	46 403	45 123	46 475	46 306
$3s4p \ ^3P_0^o$	47 841	46 919	48 079	47 756
$3s4p \ ^3P_1^o$	47 844	46 923	48 082	47 760
$3s4p \ ^3P_2^o$	47 851	46 929	48 090	47 767
$3s3d \ ^3D_3$	47 957	46 973	48 227	47 880
$3s3d \ ^3D_2$	47 957	46 973	48 227	47 879
$3s3d \ ^3D_1$	47 957	46 973	48 227	47 879
$3s4p \ ^1P_1^o$	49 347	48 490	49 672	49 277
$3s4d \ ^1D_2$	53 135	52 041	53 337	53 037
$3s4d \ ^3D_1$	54 192	53 243	54 486	54 111
$3p^2 \ ^3P_0$	57 813	56 182	58 003	57 706

involves a summation over the virtual orbitals; we have therefore used the basis $32spdfg$ for this part of the calculation, which is essentially complete.

Table I 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 II. Table III presents the resulting SMS level shift constants, k_{SMS} of Eq. (1). In each table we present results of the pure CI calculation (which agree with our previous calculation Ref. [13]), as well as calculations including Σ_1 only, and both Σ_1 and Σ_2 .

It is worth noting a few points. First, 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 work for atoms with several valence electrons these have either been neglected entirely or included using a simple fitting procedure based on the polarizability of the core [17].

The core-valence effects are much more important for the SMS calculation. In particular the single-valence-electron diagrams (included in Σ_1) can improve accuracy drastically in cases where the pure CI method is not very good. Although Σ_2 is important for energy calculation, it appears to make little difference to k_{SMS} . This is easily understood since the most important two-body diagram (the direct diagram, corresponding to the screening of the electron-electron interaction by the core electrons) makes no contribution to the SMS. The exchange diagrams in Σ_2 do have an effect, but this is much smaller than the one-body contribution.

In Table IV we compare experimental and calculated frequency shifts between isotopes ^{26}Mg and ^{24}Mg ($\delta\nu^{26,24}$). We compare the SMS part only, which is extracted from experiment by subtracting the NMS. We have ignored the volume

TABLE II. Relativistic shift of Mg I transitions relative to the ground state ($3s^2^1S_0$).

Upper level	Energy (cm ⁻¹)	q (cm ⁻¹)		
		CI	CI+ Σ_1	CI+ $\Sigma_1+\Sigma_2$
$3s3p^3P_0^o$	21 850	61	66	68
$3s3p^3P_1^o$	21 870	81	88	89
$3s3p^3P_2^o$	21 911	122	132	133
$3s3p^1P_1^o$	35 051	86	94	94
$3s4s^3S_1$	41 197	55	61	61
$3s4s^1S_0$	43 503	60	65	66
$3s3d^1D_2$	46 403	117	123	122
$3s4p^3P_0^o$	47 841	67	73	73
$3s4p^3P_1^o$	47 844	70	76	77
$3s4p^3P_2^o$	47 851	77	83	84
$3s3d^3D_3$	47 957	79	85	86
$3s3d^3D_2$	47 957	79	85	86
$3s3d^3D_1$	47 957	79	85	86
$3s4p^1P_1^o$	49 347	80	86	87
$3s4d^1D_2$	53 135	94	101	102
$3s4d^3D_1$	54 192	73	79	80
$3p^2^3P_0$	57 813	198	214	214

shift for simplicity; it is approximately 20–30 MHz, which is less than the experimental uncertainty in most cases and is of the order of the error in our SMS calculations.

Also presented in Table IV, for a theoretical comparison, are the results of Veseth (Ref. [23]) and Jönsson *et al.* (Ref. [24]). Veseth used nonrelativistic many-body perturbation

TABLE III. Calculations of the specific mass shift constants k_{SMS} for Mg I transitions to the ground state (in GHz amu).

Upper level	Energy (cm ⁻¹)	k_{SMS} (GHz amu)		
		CI	CI+ Σ_1	CI+ $\Sigma_1+\Sigma_2$
$3s3p^3P_0^o$	21 850	-378	-487	-492
$3s3p^3P_1^o$	21 870	-377	-486	-491
$3s3p^3P_2^o$	21 911	-375	-485	-489
$3s3p^1P_1^o$	35 051	231	120	134
$3s4s^3S_1$	41 197	43	-59	-49
$3s4s^1S_0$	43 503	13	-94	-85
$3s3d^1D_2$	46 403	-345	-500	-477
$3s4p^3P_0^o$	47 841	-17	-136	-126
$3s4p^3P_1^o$	47 844	-16	-136	-126
$3s4p^3P_2^o$	47 851	-16	-136	-126
$3s3d^3D_3$	47 957	52	-87	-77
$3s3d^3D_2$	47 957	52	-87	-77
$3s3d^3D_1$	47 957	52	-87	-77
$3s4p^1P_1^o$	49 347	5	-120	-108
$3s4d^1D_2$	53 135	-100	-246	-239
$3s4d^3D_1$	54 192	32	-99	-88
$3p^2^3P_0$	57 813	-225	-469	-464

theory within the algebraic approximation to calculate the isotope shift to third order for some transitions. Jönsson *et al.* used a nonrelativistic multiconfiguration Hartree-Fock approach, which allowed for both core and valence excitations in the CI.

An understudied transition that is seen in quasar absorp-

TABLE IV. Comparison of our calculated SMS with that extracted from experiment for several transitions (in MHz). The isotope shifts are between ^{26}Mg and ^{24}Mg . Also presented are the results of Refs. [23,24] for theoretical comparison. We have neglected the field shift; it is of the order of 20–30 MHz.

Transition	λ (Å)	IS (expt.)	NMS	SMS			Expt.	Ref.[23]	Ref.[24]
				CI	CI+ Σ_1	CI+ $\Sigma_1+\Sigma_2$			
$3s^2^1S_0 \rightarrow 3s3p^3P_1^o$	4572	2683(0) ^a	1153	1208	1559	1573	1530	1378	1666
$3s^2^1S_0 \rightarrow 3s3p^1P_1^o$	2853	1412(21) ^b 1390(31) ^c	1848	-740	-383	-428	-436		-409
$3s3p^3P_0^o \rightarrow 3s4s^3S_1$	5169	-396(6) ^d	1020	-1347	-1371	-1419	-1416		
$3s3p^3P_1^o \rightarrow 3s4s^3S_1$	5174	-390(5) ^d	1019	-1345	-1369	-1416	-1409		
$3s3p^3P_2^o \rightarrow 3s4s^3S_1$	5185	-390(7) ^d	1017	-1339	-1363	-1411	-1407		
$3s3p^3P_1^o \rightarrow 3p^2^3P_0$	2782	1810(80) ^e	1895	-486	-56	-86	-85		
$3s3p^3P_0^o \rightarrow 3s3d^3D_1$	3830	60(15) ^b	1376	-1377	-1283	-1329	-1316	-1269	
$3s3p^3P_1^o \rightarrow 3s3d^3D_{1,2}$	3833	61(3) ^b	1375	-1374	-1280	-1326	-1314		
$3s3p^3P_2^o \rightarrow 3s3d^3D_{1,2,3}$	3839	58(4) ^b	1373	-1368	-1274	-1321	-1315		
$3s3p^3P_1^o \rightarrow 3s4d^3D_1$	3094	420(20) ^e	1704	-1309	-1241	-1291	-1284		
$3s3p^1P_1^o \rightarrow 3s4d^1D_2$	5530	2107(15) ^d	953	1059	1173	1195	1154		

^aSterr *et al.* [25].^bHallstadius [26].^cLe Boiteux *et al.* [27].^dHallstadius and Hansen [28].^eNovero *et al.* [29].

tion spectra is the 2026 Å line of Mg I ($3s^2\ ^1S_0 \rightarrow 3s4p\ ^1P_1^o$). From Table III, we calculate the isotope shift of this line as $\delta\nu^{26,24}=2950(50)$ MHz (the error here is based on the absence of field shift as well as the incompleteness of saturation of the basis set used to calculate k_{SMS}).

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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