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Isotope-shift calculations for atoms with one valence electron

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This work presents a method for the *ab initio* calculation of isotope shift in atoms and ions with one valence electron above closed shells. As a zero approximation, we use relativistic Hartree-Fock and then calculate correlation corrections. The main motivation for developing the method comes from the need to analyze whether different isotope abundances 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 test the isotope-shift method by comparing the calculated and experimental isotope shift for the alkali-metal and alkali-metal-like atoms Na, Mg II, K, Ca II and Ba II. The agreement is found to be good. We then calculate the isotope shift for some astronomically relevant transitions in Si II and Si IV, Mg II, Zn II, and Ge II.

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I. INTRODUCTION

Recent studies of quasar absorption spectra 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 different to those on earth. This 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 is available for only a very few of them. Therefore, accurate calculations are needed to make the most comprehensive analysis possible.

Another motivation for accurate isotope-shift calculations comes from the possibility to use isotope shift to study atomic nuclei. Comparing calculated and measured IS allows one to find the change in nuclear charge distribution from one isotope to another. Studying IS for these purposes has long history, for a good review and tables see, e.g., Ref. [3] or for more recent values in many atoms and ions [4]. However, any progress in the accuracy of calculations is of significant importance.

Isotope shift is also important in searching for small, charged black holes. The mass deficit of the observable universe (dark matter) may be explained by supposing the existence of nonvanishing ‘‘elementary’’ black holes of the Planck mass. Such black holes may have an electric charge, giving rise to the possibility of an atom made from electrons orbiting a positively charged black-hole instead of a nucleus. Such black-hole atoms would have spectra shifted with respect to usual nuclear atoms due to the effectively infinite mass and zero volume of the nucleus [5]. This shift is simply an extreme example of the regular isotope shift and can be calculated using the method described in this paper. A search for these spectra would verify the existence of elementary black holes or any other stable, very heavy particles, e.g., ‘‘strange matter.’’

In this paper, we develop a method for calculating the isotopic shift of atoms and ions that can be treated as a single electron above a closed-shell core. These include the alkali metals and singly ionized alkaline-earth metals, as well as other ions, such as Zn II, that are fairly well approximated by a single electron above a closed-subshell core.

We test our technique by calculating IS for light atoms and ions as well as for a relatively heavy ion, Ba II. Since different contributions dominate in light and heavy atoms and good agreement with experiment has been obtained in both cases, one can confidently say that the technique has been reliably tested. We then apply the technique to calculate isotope shift for astronomically relevant transitions in Mg II, Zn II, Ge II, Si II, and Si IV.

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. [6]). The energy shift due to recoil of the nucleus is $(1/2M)p_N^2=(1/2M)(\Sigma\mathbf{p}_i)^2$. 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 $(1/2M)\Sigma p_i^2$, which is easily calculated from the transition frequency. The SMS operator is $(1/M)\Sigma_{i<j}\mathbf{p}_i\cdot\mathbf{p}_j$, 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

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

where the normal mass shift constant is

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

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

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mass. In this paper, we develop a method for calculating the specific mass shift and field shift constants, k_{SMS} and F, respectively. It is worth noting that in this paper, we use the convention $\delta\nu^{A',A} = \nu^{A'} - \nu^{A}$.

To determine spectral shifts in black-hole atoms relative to normal atoms, one must take $A' \to \infty$, and because the black hole has effectively zero volume $\delta\langle r^2\rangle = -\langle r^2\rangle = -\frac{3}{5}R_{\text{nuc}}^2$.

A. Specific mass shift

It is well known that calculations using many-body perturbation theory (MBPT) in the residual Coulomb interaction give very poor convergence for atoms with many electrons. Therefore, all order techniques were developed in earlier works to calculate energy levels, transition amplitudes, etc. (see, e.g., Refs. [7–10]). It is natural to expect that an all order technique is needed for the isotope shift as well. In the recent work by Safronova and Johnson (Ref. [11]), the SMS was calculated to third order of MBPT. Their results verify that there is very poor convergence for this operator. A first- or second-order calculation cannot even guarantee that the sign of the final result will be correct. A third-order calculation gives the correct sign, however, it is unknown how much fourth- and higher-order diagrams contribute.

Our method is to include the specific mass shift directly into an energy calculation from the very beginning. The SMS is a two-body operator $\mathbf{p}_1 \cdot \mathbf{p}_2$ and can be added to the Coulomb potential $\tilde{Q} = 1/|\mathbf{r}_1 - \mathbf{r}_2| + \lambda \mathbf{p}_1 \cdot \mathbf{p}_2$ (see Appendix). The operator $\tilde{Q}$ replaces the Coulomb operator everywhere that it appears in an "all order" energy calculation that includes certain chains of diagrams to all orders. We vary the isotope-shift scaling factor λ and calculate the level energies E. The gradient of an E vs λ graph then gives us the SMS matrix element, usually denoted by k_{SMS}.

As a zero approximation, we use relativistic Hartree-Fock (Hartree-Fock-Dirac) method. At the Hartree-Fock stage, we include the isotope shift with the exchange potential and iterate to obtain self-consistent "dressed" wave functions. The SMS matrix element at this stage, is roughly equivalent to the first-order and second-order contributions of the one-particle operator, plus higher-order corrections from the random-phase approximation in Ref. [11] ($P^{(1)}+S^{(2)}$ in their notation). It is interesting to note that k_{SMS} at this stage does not give meaningful results, and can even be of the wrong sign (it is labeled as "HF" in Table I). We need to include correlation corrections in order to obtain any reasonable accuracy.

We include correlation effects to second order of MBPT; this approach gives good accuracy for energies. The perturbation is the difference between the exact and Hartree-Fock (HF) Hamiltonians $V = H - H_{\text{HF}}$. The many-body corrections start in second order; all first-order diagrams have been included in the self-consistent Hartree-Fock procedure. There are just four second-order diagrams, illustrated, for example, in Ref. [7]. However, now we replace the Coulomb operator in these diagrams with our two-body operator $\tilde{Q}$, and use dressed Hartree-Fock wave functions as described above. This gives our final value of k_{SMS} as listed in Table I.

TABLE I. Comparison of specific mass shift constants k_{SMS} obtained by including various contributions in the energy calculation (all in GHz amu). Our values "HF" are approximately equivalent to the values labeled "$P^{(1)}+S^{(2)}$" here and in Ref. [11].

		Ref. [11]		This work	
Ion	State	$P^{(1)}+S^{(2)}$	Final	HF	Final
Na I	$3s$	-54	54	-52	69
	$3p_{1/2}$	-67	-43	-68	-40
	$3p_{3/2}$	-67	-43	-67	-39
Mg II	$3s$		38	-171	83
	$3p_{1/2}$		-324	-408	-296
	$3p_{3/2}$		-323	-402	-290

An estimate of the size of neglected higher-order diagrams can be obtained by calculating a new value of k_{SMS} that includes some higher-order chains of diagrams. We create an operator Σ for the second-order correlation effects in each partial wave, defined by

$$\delta E_n^{(2)} = \langle n|\Sigma|n\rangle. \tag{3}$$

Σ is then added to the exchange potential in the Hartree-Fock Hamiltonian for the valence electron, $\tilde{H} = H_{\text{HF}} + \Sigma$. Thus, we calculate the single electron Brueckner orbital. We also include a scaling factor f with the Σ operator ($\Sigma \to f\Sigma$) in order to fit the experimental energy. The rescaling of Σ simulates some higher-order correlation corrections that were omitted in our calculation. Including Σ in our Hartree-Fock calculation allows us to obtain another value for k_{SMS}, and the difference between this new value and the old second-order value gives us an estimate of the error.

In Table I, we compare our results to those obtained by Safronova and Johnson (Ref. [11]) who calculated the isotope shift to third order in standard MBPT. Our values are significantly different, in particular, the Mg II $3s$ level shift is more than twice that given in Ref. [11] and also in Ref. [12], which are broadly in agreement with each other. However, we find that this difference is not so large in the $3p$-$3s$ transition due to cancellations of higher-order terms between the two levels. We compare our final results and those of Ref. [11] with experiment in Table II. Agreement is at the level of 1%, which is much smaller than our error estimates.

TABLE II. Comparison of the specific mass shift of transitions in Na and Mg II with experiment.

		SMS (MHz)		
Isotopes	Transition	Ref. [11]	This work	Experiment
$^{23-22}$Na	$3p_{1/2}-3s$	192	214(48)	215(1) 214(2)
	$3p_{3/2}$-$3s$	192	212(48)	214
$^{26-24}$Mg II	$3p_{3/2}$-$3s$	1157	1196(18)	1207(100)

[a] These values are extracted from IS experiments in Table VI.

TABLE III. Level field shifts in Ba II states. Due to a difference in the definition of *F*, the values calculated in Ref. [13] have been presented here with opposite sign.

State	Energy (cm^{-1})	F ($\mathrm{MHz/fm}^2$) Ref. [13]	F ($\mathrm{MHz/fm}^2$) This work
$6s$	−80686.87	4096	3851
$6p_{1/2}$	−60425.31	−111.1	−150.1
$6p_{3/2}$	−58734.45	−242.6	−225.4
$5d_{3/2}$	−75813.02		−1223
$5d_{5/2}$	−75012.05		−1148

Our method includes many-body diagrams that are different from those of Ref. [11], including some chains of diagrams in all orders. It is also arguably simpler to implement since it does not require term-by-term calculation of a large number of matrix elements.

B. Field shift

Our method for calculating the field shift (also called the volume shift) is similar to that used for the SMS calculation. We add a perturbation due to the field shift to the nuclear potential and then calculate the energy directly. The field shift potential is

$$\delta U(r)=\lambda[U(R+\delta R,r)-U(R,r)], \tag{4}$$

where R is the nuclear radius and $U(R,r)$ is the nuclear potential. To obtain the change in energy of a state due to the field shift, we add this potential to the nuclear potential in our Hartree-Fock calculations. By introducing a scaling factor λ, we can check linearity and increase the size of the effect. To calculate the field shift constant, we take the gradient of a level energy E vs λ graph and extract F as

$$F=\frac{\delta E_V}{\delta\langle r^2\rangle}=\frac{5}{3}\frac{1}{2R\,\delta R}\frac{dE}{d\lambda}. \tag{5}$$

Note that the field shift constant F is defined here as having opposite sign to the definition in some previous papers, e.g., Refs. [11,13]. This equation assumes that the nuclear charge distribution can be approximated as a uniformly charged sphere of radius R.

Higher-order correlation effects are smaller in the field shift than in the specific mass shift, and are localized at the nucleus. We can include them easily by creating Brueckner orbitals (solutions of the modified Hamiltonian, $H=H_{\mathrm{HF}}+\Sigma$) using a second-order Σ operator, defined in Eq. (3). The field shift is proportional in first order to the square of the wave function at the nucleus. Hence, we can include higher-order effects quite simply by multiplying the matrix element by the square of the ratio of the Brueckner wave function to the Hartree-Fock wave function at the nucleus,

$$\frac{F_{\mathrm{HF}+\Sigma}}{F_{\mathrm{HF}}}=\left|\frac{\psi_{\mathrm{HF}+\Sigma}(0)}{\psi_{\mathrm{HF}}(0)}\right|^2. \tag{6}$$

TABLE IV. Calculated SMS and field shift constants in Ba II transitions.

Transition	Wavelength (nm)	k_{SMS} (GHz amu)	F ($\mathrm{MHz/fm}^2$)
$6p_{1/2}$-$6s$	493	105	−4001
$6p_{3/2}$-$6s$	455	257	−4077
$5d_{5/2}$-$6s$	1762	−550	−4999
$6p_{1/2}$-$5d_{3/2}$	650	653	1073
$6p_{3/2}$-$5d_{3/2}$	585	805	997
$6p_{3/2}$-$5d_{5/2}$	614	807	922

We tested this in Ba II, as well as in lighter atoms, because in barium the field shift dominates over the mass shift, and there is a lot of experimental data to compare with. Our results for field shift constants in Ba II were found to be consistent within a few percent of the previous theoretical work by Måartensson-Pendrill (Table III). In the same paper, Ref. [13], they say that they have underestimated the $6p_{1/2}$ field shift constant by around 7%, based on the difference between experimental and theoretical calculations of the hyperfine *A* constant. Also, their $6s$ constant is said to be overestimated, leading to a corrected value of $F_{6p_{3/2}}-6s=-4.20(13)\ \mathrm{GHz/fm}^2$. These corrected values are in better agreement with the *ab initio* values obtained in this work ($F_{6p_{3/2}-6s}=-4.076\ \mathrm{GHz/fm}^2$).

Using King plots [14], we can extract the ratios of field shift constants for different transitions, provided we have experimental data for a number of different isotopes. We ompare our calculated values of these ratios (Table IV) with those obtained by combining the data of several different experiments and transitions in Table V. Our values were found to be consistent with this experiment to within 5%. We have used a simple weighted least-squares fit to obtain an

TABLE V. Ratios of field shift constants in Ba II states. In the second column, we list the measured values obtained using King plots. In some cases, we obtain the ratio ourselves by combining the results of two separate studies.

Transitions (α/β)	F_α/F_β This work	F_α/F_β Experiment
$6p_{1/2}$-$6s/6p_{3/2}$-$6s$	0.982	0.975(3) [a]
$6p_{3/2}$-$6s/6p_{3/2}$-$5d_{5/2}$	−4.42	−4.50(6) [b, c]
$6p_{3/2}$-$6s/5d_{5/2}$-$6s$	0.816	0.82(4) [b, d]
$5d_{5/2}$-$6s/6p_{3/2}$-$5d_{5/2}$	−5.42	−5.5(3) [c, d]
$6p_{1/2}$-$5d_{3/2}/6p_{3/2}$-$5d_{3/2}$	1.076	1.087(4) [c]
$6p_{3/2}$-$5d_{5/2}/6p_{3/2}$-$5d_{3/2}$	0.925	0.961(3) [c]
$6p_{3/2}$-$5d_{3/2}/6p_{3/2}$-$6s$	−0.245	−0.2312(6) [c]

[a] Wendt *et al.* [15].

[b] Wendt *et al.* [16].

[c] Villemoes *et al.* [17].

[d] Zhao *et al.* [18].

TABLE VI. Comparison of experimental values of the specific mass shift with calculated theoretical values. The experimental values were extracted by subtracting the NMS and field shift (FS) from the experimental IS.

Isotopes	Transition	Energy (cm^{-1})	IS (expt.) (MHz)	NMS (MHz)	FS (MHz)	SMS (MHz) This work	SMS (MHz) Experimental
$^{23-22}$Na	$3p_{1/2}$-$3s$	16956.18	758.5(7) [a]	551	−8	214(48)	215(1)
			756.9(1.9) [b]				214(2)
	$3p_{3/2}$-$3s$	16973.38	757.72(24) [c]	552	−8	212(48)	214
$^{26-24}$Mg II	$3p_{3/2}$-$3s$	35760.97	3050(100) [d]	1185	−42	1196(18)	1207(100)
$^{41-39}$K	$4p_{1/2}$-$4s$	12985.17	235.25(75) [e]	267	−13(5)	−32(21)	−19(6)
	$4d_{1/2}$-$4s$	27398.11	585(9) [f]	564	−13(5)	20(30)	34(13)
$^{43-40}$Ca II	$4p_{1/2}$-$4s$	25191.54	706(42) [g]	723	−36(3)	22(1)	19(45)
			672(9) [h]				−15(11)
			685(36) [i]				−2(39)
	$4p_{3/2}$-$4s$	25414.43	713(31) [g]	729	−36(3)	−5(1)	20(34)
			677(19) [h]				−16(22)
			685(36) [i]				−8(39)
	$3d_{3/2}$-$4s$	13650.21	4180(48) [g]	392	−47(4)	3502(217)	3835(52)
	$3d_{5/2}$-$4s$	13710.90	4129(10) [g]	393	−47(4)	3487(215)	3783(14)
	$4p_{1/2}$-$3d_{3/2}$	11541.33	−3464.3(3.0) [j]	331	12(1)	−3479(218)	−3807(4)
			−3483(40) [g]				−3826(41)
	$4p_{3/2}$-$3d_{3/2}$	11764.22	−3462.4(2.6) [j]	337	12(1)	−3507(217)	−3811(4)
			−3446(20) [g]				−3795(21)
	$4p_{3/2}$-$3d_{5/2}$	11703.53	−3465.4(3.7) [j]	336	12(1)	−3492(216)	−3813(5)
			−3427(33) [g]				−3774(34)

[a] Pescht *et al.* [19].
[b] Huber *et al.* [20].
[c] Gangrsky *et al.* [21].
[d] Drullinger *et al.* [22].
[e] Touchard *et al.* [23].
[f] Hörbäck *et al.* [24].
[g] Kurth *et al.* [25].
[h] Extracted from Måartensson-Pendrill *et al.* [26].
[i] Maleki and Goble [27].
[j] Nörtershäuser *et al.* [28].

experimental value for the ratio F_{455}/F_{614}. A two-point formula was used for ratios involving the 1762-nm transition as experimental data exists only for the $\delta\nu^{134,138}$ and $\delta\nu^{136,138}$ isotope shifts [18]. Other ratios were extracted by the groups that performed the experiments, with much higher accuracy.

C. Alkali metals and alkaline-earth metals

We compare our results with experimental data for alkali-metal atoms and ionized alkaline-earth metals in Table VI. In these systems, it is more valuable to compare only the specific mass shift with those extracted from experiment than to compare the entire isotope shift. This is because the mass shift dominates strongly in these atoms and ions, and also because the SMS is generally considered more difficult to calculate. We have removed the field shift and the normal mass shift from the experimental values of the isotopic shift in order to obtain an experimental value for the specific mass shift. The field shift values used in Table VI were calculated using the above method. While our calculation of F has been shown to be good, the field shift also depends on having knowledge of $\delta\langle r^2\rangle$ for the relevant isotopes.

For Na, we use the value quoted in Ref. [11] of $\delta\langle r^2\rangle^{23,22}=0.205(3)\ \mathrm{fm}^2$. This value is only from an empirical fit, and should not be trusted too far. The field shift is very small in this atom, so the errors do not matter too much. For Mg II, we have used the value $\delta\langle r^2\rangle^{26,24}=0.55\ \mathrm{fm}^2$ from another empirical fit, the equation $R_{\mathrm{nuc}}=1.1A^{1/3}$ fm. This is a poor approximation, but in this case the field shift is small even in relation to the error in the experimental isotope shift. In Table VI, we have not included an error contribution for the field shift in either of these atoms, since we really do not know how accurate these approximations are.

The values of $\delta\langle r^2\rangle$ are known for K and Ca II from muonic x-ray experiments, allowing us to calculate the field shift much more accurately. This is fortunate because the SMS is relatively small for the p-s transitions in these atoms, and hence, the field shift plays a much larger role. We use the values $\delta\langle r^2\rangle^{41,39}=0.117(40)\ \mathrm{fm}^2$ for K from Ref. [29], and $\delta\langle r^2\rangle^{43,40}=0.1254(32)\ \mathrm{fm}^2$ for Ca II from Ref. [30]. In Ca II the change in mean square nuclear radius is given to high precision, so we have included an additional error of 5% in the field shift that comes from the constant F. This is a pessimistic estimate of error based on the accuracy we achieved calculating F for transitions in Ba II.

Table VI shows that our method can reliably calculate the isotope shift in alkali-metal atoms and singly ionized alkaline-earth metals, including those transitions with a large specific mass shift.

TABLE VII. Mass and field shift constants for some useful transitions.

Ion	Transition	F (MHz/fm^2)	k_{NMS} (GHz amu)	k_{SMS} (GHz amu)
Mg II	$3p_{1/2}$-$3s$	-127	-587	$-373(12)$
	$3p_{3/2}$-$3s$	-127	-588	$-373(6)$
Si II	$4s$-$3p_{1/2}$	171	-1077	1257(29)
	$4s$-$3p_{3/2}$	171	-1072	1243(28)
Si IV	$3p_{1/2}$-$3s$	-484	-1172	$-1535(11)$
	$3p_{3/2}$-$3s$	-485	-1180	$-1505(7)$
Zn II	$4p_{1/2}$-$4s$	-1596	-797	$-1310(69)$
	$4p_{3/2}$-$4s$	-1596	-812	$-1266(69)$
Ge II	$5s$-$4p_{1/2}$	1088	-1026	1046(69)
	$5s$-$4p_{3/2}$	1083	-997	960(62)

III. RESULTS

We have shown that our method works in atoms for which experimental data are available (Sec. II). In Table VII, we tabulate values for the mass and field shift constants for some astronomically useful transitions. We have not given errors for F, however, we can say that they are less than 5% based on comparison of calculation with experiment in Ba II.

In Table VIII, we present the results of isotope-shift calculations between common isotopes of astronomically important ions. We have used the IS constants presented in Table VII with Eq. (1) in order to calculate the isotope shift between particular isotopes. Just before submission of this paper, results of measurements for Zn II were brought to our attention [31]. These results matched our prediction extremely well.

In Ge II and Si II, the specific mass shift cancels the normal mass shift entirely, making the field shift, and hence $\delta\langle r^2\rangle$, important. We have just used the empirical formula $R_{\text{nuc}}=1.1A^{1/3}$ fm^2 to obtain values of $\delta\langle r^2\rangle$ in these ions. This is extremely rough, and although it seems to work in Zn II to within a 20% accuracy based on the experimental data given, we really do not know if this holds for Si and Ge at all. In the Si IV transitions presented, it is less important to have good values for the field shift because there is no cancellation between the NMS and SMS.

TABLE VIII. Summary of isotope shift values for astronomically relevant alkali-metals-like ions. The experimental value for the $4p_{3/2}$-$4s$ transition in Zn II is 676(6) MHz as quoted in Ref. [31]. We have presented two errors, the first is our uncertainty in k_{SMS} and the second is the uncertainty in our field shift, which is mainly due to lack of knowledge of $\delta\langle r^2\rangle$. A negative shift means that the sign is opposite to the normal mass shift.

Isotopes	Transition	Energy (cm^{-1})	Isotope shift (MHz)
$^{30-28}$Si II	$4s$-$3p_{1/2}$	65495.1	$-375(70)(11)$
	$4s$-$3p_{3/2}$	65208.1	$-351(67)(11)$
$^{30-28}$Si IV	$3p_{1/2}$-$3s$	71289.6	6294(26)(31)
	$3p_{3/2}$-$3s$	71749.9	6241(18)(31)
$^{66-64}$Zn II	$4p_{1/2}$-$4s$	48480.6	653(32)(78)
	$4p_{3/2}$-$4s$	49354.4	632(33)(79)
$^{74-70}$Ge II	$5s$-$4p_{1/2}$	62402.4	491(53)(101)
	$5s$-$4p_{3/2}$	60635.3	533(48)(101)

IV. CONCLUSION

We have presented a method for the calculation of the isotope shift in atoms and ions that can be approximated as having one valence electron above a closed shell. Our results are shown to be in good agreement with isotope-shift experiments in both light and heavy atoms, which are good tests for the mass shift, and field shift respectively.

We have used the method to predict values of the isotope shift in astronomically relevant transitions in Si II and Si IV, Mg II, Zn II, and Ge II. Recent experiments measured the isotope shift of a p-s transition in ZnII, and the results were in excellent agreement with our prediction. These values are needed in order to examine systematic effects in observations of spectral line shifts in quasar absorption spectra that suggest a variation in α [2]. Our calculations could help provide another explanation for the observed shifts, depending on whether isotopic abundances were different in gas clouds in the early universe. Alternatively, our calculations may strengthen the arguments in support of a varying α.

Further work needs to be done in order to obtain the isotope shift for more complex atoms with more than one electron in their outer shell. The general method of including the isotope-shift operator with the two-body Coulomb operator may be used in such cases, although the energy calculation itself is more complicated.

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APPENDIX: MATRIX ELEMENT OF THE TWO-BODY OPERATOR

The two-body operator used is this work is the sum of the Coulomb interaction operator and the "rescaled" SMS operator (atomic units):

$$\tilde{Q}=\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+\lambda\mathbf{p}_1\cdot\mathbf{p}_2\equiv\sum_k\tilde{Q}_k, \tag{A1}$$

where λ is the scaling factor, $\mathbf{p}=-i\boldsymbol{\nabla}$ is electron momentum, and

$$\tilde{Q}_k=\frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}Y_k(\mathbf{n}_1)Y_k(\mathbf{n}_2)+\lambda\mathbf{p}_1\cdot\mathbf{p}_2\delta_{k1}. \tag{A2}$$

We use the following form for the single-electron wave function:

$$\psi(\mathbf{r})_{jlm}=\frac{1}{r}\begin{pmatrix} f(r)\Omega(\mathbf{n})_{jlm} \\ i\alpha g(r)\tilde{\Omega}(\mathbf{n})_{jlm}\end{pmatrix}. \tag{A3}$$

Here, $\alpha = 1/137.036$ is the fine-structure constant and $\tilde{\Omega}(\mathbf{n})_{jlm} = -(\boldsymbol{\sigma}\cdot\mathbf{n})\Omega(\mathbf{n})_{jlm}$.

The matrix element of operator (A2) with wave functions (A3) has the form

$$\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)|\tilde{Q}_k|\psi_3(\mathbf{r}_1)\psi_4(\mathbf{r}_2)\rangle = C_k(R_k - \lambda P_1\delta_{k1}), \tag{A4}$$

where the angular factor C_k is the same for both operators

$$\begin{aligned} C_k = {} & (-1)^{q+m_1+m_2}\begin{pmatrix} j_1 & k & j_3 \\ -m_1 & q & m_3 \end{pmatrix}\begin{pmatrix} j_2 & k & j_4 \\ -m_2 & -q & m_4 \end{pmatrix} \\ & \times(-1)^{j_1+j_2+j_3+j_4+1} \\ & \times\sqrt{(2j_1+1)(2j_2+1)(2j_3+1)(2j_4+1)} \\ & \times\begin{pmatrix} j_1 & j_3 & k \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix}\begin{pmatrix} j_2 & j_4 & k \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \\ & \times\xi(l_1+l_3+k)\xi(l_2+l_4+k), \end{aligned}$$

$$\xi(x) = \begin{cases} 1 & \text{if } x \text{ is even,} \\ 0 & \text{if } x \text{ is odd,} \end{cases} \tag{A5}$$

R_k is radial Coulomb integral

$$\begin{aligned} R_k = {} & \int_0^\infty \frac{r_<^k}{r_>^{k+1}}[f_1(r_1)f_3(r_1) + \alpha^2 g_1(r_1)g_3(r_1)] \\ & \times[f_2(r_2)f_4(r_2) + \alpha^2 g_2(r_2)g_4(r_2)]dr_1 dr_2, \end{aligned} \tag{A6}$$

while P_1 is radial matrix element of the SMS operator

$$\begin{aligned} P_1 &= p_{13}p_{24}, \\ p_{ab} &= A_{ab}\delta_{l_a l_b+1} + B_{ab}\delta_{l_a l_b-1}, \\ A_{ab} &= \int_0^\infty f_a\left(\frac{d}{dr} - \frac{l_a}{r}\right)f_b dr, \\ B_{ab} &= \int_0^\infty f_a\left(\frac{d}{dr} + \frac{l_b}{r}\right)f_b dr. \end{aligned} \tag{A7}$$

[1] J.K. Webb, V.V. Flambaum, C.W. Churchill, M.J. Drinkwater, and J.D. Barrow, Phys. Rev. Lett. **82**, 884 (1999); J.K. Webb *et al.*, *ibid.* **87**, 091301 (2001); M.T. Murphy *et al.*, Mon. Not. R. Astron. Soc. **327**, 1208 (2001); **327**, 1237 (2001); J.K. Webb, M.T. Murphy, V.V. Flambaum, and S.J. Curran, Astrophys. Space Sci. **283**, 565 (2003).

[2] M.T. Murphy, J.K. Webb, V.V. Flambaum, C.W. Churchill, and J.X. Prochaska, Mon. Not. R. Astron. Soc. **327**, 1223 (2001); M.T. Murphy, J.K. Webb, V.V. Flambaum, and S.J. Curran, Astrophys. Space Sci. **283**, 577 (2003); M. T. Murphy, J. K. Webb, and V. V. Flambaum, Mon. Not. R. Astron. Soc. (to be published); e-print astro-ph/0306483.

[3] K. Heilig and A. Steudel, At. Data Nucl. Data Tables **14**, 613 (1974).

[4] P. Aufmuth, K. Heilig, and A. Steudel, At. Data Nucl. Data Tables **37**, 455 (1987).

[5] V.V. Flambaum and J.C. Berengut, Phys. Rev. D **63**, 084010 (2001).

[6] I.I. Sobel'man, *Introduction to the Theory of Atomic Spectra* (Pergamon, New York, 1972).

[7] V.A. Dzuba, V.V. Flambaum, P.G. Silvestrov, and O.P. Sushkov, J. Phys. B **20**, 1399 (1987).

[8] V.A. Dzuba, V.V. Flambaum, and O.P. Sushkov, Phys. Lett. A **140**, 493 (1989).

[9] V.A. Dzuba, V.V. Flambaum, A.Ya. Kraftmakher, and O.P. Sushkov, Phys. Lett. A **142**, 373 (1989).

[10] S.A. Blundell, W.R. Johnson, and J. Sapirstein, Phys. Rev. A **43**, 3407 (1991).

[11] M.S. Safronova and W.R. Johnson, Phys. Rev. A **64**, 052501 (2001).

[12] L. Veseth, J. Phys. B **18**, 3463 (1985).

[13] A-M. Mårtensson-Pendrill and A. Ynnerman, J. Phys. B **25**, L551 (1992).

[14] W.H. King, J. Opt. Soc. Am. **53**, 638 (1963).

[15] K. Wendt *et al.*, Z. Phys. A **318**, 125 (1984).

[16] K. Wendt *et al.*, Z. Phys. A **329**, 407 (1988).

[17] P. Villemoes, A. Arnesen, F. Heijkenskjöld, and A. Wännström, J. Phys. B **26**, 4289 (1993).

[18] X. Zhao, N. Yu, H. Dehmelt, and W. Nagourney, Phys. Rev. A **51**, 4483 (1995).

[19] K. Pescht, H. Gerhardt, and E. Matthias, Z. Phys. A **281**, 199 (1977).

[20] G. Huber *et al.*, Phys. Rev. C **18**, 2342 (1978).

[21] Yu.P. Gangrsky *et al.*, Eur. Phys. J. A **3**, 313 (1998).

[22] R.E. Drullinger, D.J. Wineland, and J.C. Bergquist, Appl. Phys. **22**, 365 (1980).

[23] F. Touchard *et al.*, Phys. Lett. **108B**, 169 (1982).

[24] S. Hörbäck, A-M. Pendrill, L. Pendrill, and M. Pettersson, Z. Phys. A **318**, 285 (1984).

[25] F. Kurth *et al.*, Z. Phys. D: At., Mol. Clusters **34**, 227 (1995).

[26] A-M. Mårtensson-Pendrill *et al.*, Phys. Rev. A **45**, 4675 (1992).

[27] S. Maleki and A.T. Goble, Phys. Rev. A **45**, 524 (1992).

[28] W. Nörtershäuser *et al.*, Eur. Phys. J. D **2**, 33 (1998).

[29] H.D. Wohlfahrt *et al.*, Phys. Rev. C **23**, 533 (1981).

[30] C.W.P. Palmer, P.E.G. Baird, S.A. Blundell, and J.R. Brandenberger, J. Phys. B **17**, 2197 (1984).

[31] K. Matsubara *et al.*, Appl. Phys. B: Lasers Opt. **76**, 209 (2003).