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Perturbation theory for the Stark effect in the hyperfine structure of alkali-metal atoms*†

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We have studied the quadratic Stark effect on the hyperfine structure in the ground states of the alkali-metal atoms, lithium through cesium. In evaluating the leading perturbation terms, we have utilized two sets of first-order wave functions, corresponding respectively to perturbations of the atomic wave functions by the electric field and by the nuclear moment. The perturbed wave-functions were obtained by solving the appropriate differential equations in first-order perturbation theory. The theoretical results agree very well with the recent experimental data for the entire series of alkali-metal atoms. A discussion of the relation of our theoretical results to earlier ones in some of the alkali-metal atoms is also presented.

I. INTRODUCTION

The shift in the hyperfine transition frequency in the ground states of hydrogen and the alkali-metal atoms due to the presence of a uniform electric field has been studied by various investigators. This hyperfine Stark shift (HSS) has been measured in hydrogen by Fortson *et al.*,[1] in potassium by Snider,[2] and in cesium by Haun and Zacharias,[3] and recently in all the alkali-metal atoms by Mowat.[4]

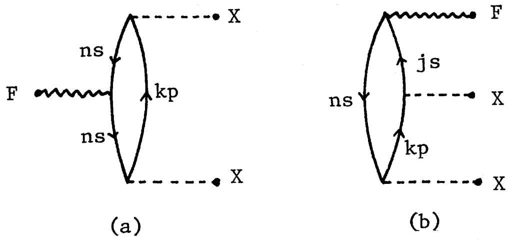
A theoretical investigation of the HSS in the alkali-metal atoms is of great interest, since it requires an accurate knowledge of the change in the electronic wave function near the nucleus due to the presence of the electric field. It would also be interesting to see whether the good agreement between theory and experiment that was found for hydrogen[5,6] holds for other alkali atoms. A number of theoretical calculations have been carried out in some of the alkali atoms with varying degrees of success.[7-11]

In the recent diagrammatic many-body perturbation analysis for the HSS in the ground state of lithium by Rodgers *et al.*,[10] it was found that the major contribution to the HSS of lithium is from the two diagrams shown in Fig. 1, one representing the effect of renormalization of the wave function and the other the effect of *s* admixture through the second-order perturbation due to the electric field. This feature has also been observed in the subsequent study on sodium and potassium by Kelly *et al.*[11]

Besides the major diagrams shown in Fig. 1, higher-order diagrams involving up to two orders in electron-electron interaction have also been studied in the literature.[10] These diagrams incorporate consistency and correlation effects on the hyperfine Stark shift. It was found that the major consistency and correlation effects were associated with the hyperfine vertex in Fig. 1(a), and that they could be included by using the experimental hyperfine constant for this vertex.

In view of the above finding, we felt that it would be interesting to calculate the diagrams 1(a) and 1(b) for the HSS in the entire series of alkali atoms for which data are available.[2-4] Since diagrams 1(a) and 1(b) basically involve perturbations in the wave functions due to the electric field and nuclear magnetic moment through the hyperfine interaction, one can calculate these diagrams using perturbed functions obtained from solutions of appropriate differential equations[12-14] in first-order perturbation theory instead of summations over excited states. Such perturbed functions from solutions of appropriate differential equations are used in work on electronic polarizabilities[12,13] and exchange core polarization contributions to hyperfine constants.[14]

In Sec. II, this perturbation procedure that we have utilized for calculating the hyperfine transition frequency in the presence of the electric field



(a) (b)

FIG. 1. Two leading diagrams for the HSS of alkali atoms. *F* represents the Fermi-contact interaction and *X* the electric field vertex. *ns* denotes the valence *s* orbital involved.

is described together with a brief description of the perturbation procedure used for obtaining the perturbed wave functions due to perturbations by the uniform electric field and the nuclear moment. The results are presented at the end of Sec. II. Section III contains discussion of the results and a comparison with experiment and earlier theoretical calculations.

II. THEORY AND PROCEDURE

The method that we utilize here is very similar to one that has been adopted for studying electron-electron interaction effects[15] on the shielding of the field gradient due to external charges at the site of the nucleus in ions. In effect, what is done is to evaluate the important diagrams of many-body perturbation theory using the perturbed wave functions obtained out of differential equations, rather than summation over excited states. Thus contributions from the diagrams 1(a) and 1(b) to the HSS can be written as

$$\delta E(1\mathrm{a}) = -\langle \phi_{ns} | F | \phi_{ns} \rangle \langle \delta\phi_{ns\to p} | \delta\phi_{ns\to p} \rangle \ , \tag{1}$$

$$\delta E(1\mathrm{b}) = 2\langle \delta\phi_{ns\to p} | X | \Delta\phi_{ns\to s} \rangle \ , \tag{2}$$

where F and X are given by

$$F = \frac{16\pi}{3} \frac{\mu_B \mu_N}{I} \vec{\mathrm{I}} \cdot \vec{\mathrm{S}} \delta(\vec{\mathrm{r}}) \ , \tag{3}$$

$$X = -\mathcal{E} r \cos\theta \ , \tag{4}$$

and represent the Fermi-contact interaction and the perturbation due to the uniform external electric field $\vec{\mathcal{E}}$, respectively. In Eqs. (1) and (2), we have used ϕ_{ns} for the unperturbed valence s-state wave function, $\delta\phi_{ns\to p}$ for the first-order perturbed wave function due to the electric field, and $\Delta\phi_{ns\to s}$ for the first-order wave function perturbed by the nuclear moment. In Eq. (3), μ_B is the Bohr magneton, μ_N the nuclear magnetic moment, and $\vec{\mathrm{I}}$ and $\vec{\mathrm{S}}$ denote nuclear and electronic spin angular momentum, respectively. In many-body perturbation theory,[10,11] the first-order perturbed wave functions $\delta\phi_{ns\to p}$ and $\Delta\phi_{ns\to s}$ are given in terms of excited states, namely,

$$\delta\phi_{ns\to p} = \sum_k \frac{\langle \phi_{kp} | X | \phi_{ns} \rangle}{E_{ns} - E_{kp}} \phi_{kp} \ , \tag{5}$$

$$\Delta\phi_{ns\to s} = \sum_k \frac{\langle \phi_{ks} | F | \phi_{ns} \rangle}{E_{ns} - E_{ks}} \phi_{ks} \ , \tag{6}$$

where E_{nl} denotes single-particle energies. The summations in Eqs. (5) and (6) are to be replaced by integrations for continuum states.

In the differential-equation approach, however, they are obtained directly by integrating the differential equations for the first-order perturbed wave functions. These equations are given by[13,14]

$$(H_0 - E_{ns})\delta\phi_{ns\to p} = -f(r) X \phi_{ns} \ , \tag{7}$$

$$(H_0 - E_{ns})\Delta\phi_{ns\to s} = (E_1 - F)\phi_{ns} \ , \tag{8}$$

where

$$E_1 = \langle \phi_{ns} | F | \phi_{ns} \rangle \tag{9}$$

and $f(r)$ is the factor introduced by Sandars[16] to include the shielding effect of the external electric field by the ion core.

If one used for the unperturbed wave functions ϕ_{ns}, the appropriate Hartree-Fock wave functions and replaced $f(r)$ in Eq. (7) by unity, one would really be evaluating the diagrams 1(a) and 1(b). However, the wave functions ϕ_{ns} used in the present work have been determined[13] in empirical potentials, which reproduce the observed ionization potentials of the valence electrons of alkali atoms. The factor $f(r)$ was introduced,[16] in polarizability calculations, to incorporate in an approximate way, the shielding effect of the core electrons on the electric field acting on the valence electrons. In view of these last two features, the present calculation perhaps can be considered to incorporate some of the consistency and correlation effects in other diagrams[10] besides those in Figs. 1(a) and 1(b), although the exact contributions from such effects by this procedure is not precisely known. As stated in the Introduction, we have used the experimental hyperfine constant at the hyperfine vertex in Fig. 1(a), which incorporates exchange core polarization, correlation and relativistic effects associated with this vertex. The perturbed functions $\delta\phi_{ns\to p}$ used in our calculations[13] have been found[12] to be in good agreement with recent experimental results for polarizabilities.[17]

Our theoretical results are expressed in terms of the parameter k, which is related to the HSS (in frequency units) as

$$\begin{aligned} \delta\nu &= [(\delta E)_{F=I+1/2} - (\delta E)_{F=I-1/2}]/h \\ &= -k\mathcal{E}^2 \times 10^{-6}\ \mathrm{Hz/(V/cm)^2} \ , \end{aligned} \tag{10}$$

$\mathcal{E}$ denoting the electric field. Table I contains the theoretical results for k from the two diagrams 1(a) and 1(b).

III. DISCUSSION

The relative contributions to k from the diagrams 1(a) and 1(b) are found to be 60% and 40%, respectively, of the total calculated results for the entire series of atoms, and these total theoretical results are now in very good agreement with experiment.[4]

For Li, Na, and K, we can compare our results

TABLE I. Contributions of the diagrams in Fig. 1 to k in Eq. (10) for alkali atoms.

System	1(a)	1(b)	Total	k_{expt} [a]
^{7}Li	0.0376	0.0219	0.0595	0.061(2)
^{23}Na	0.0622	0.0575	0.1197	0 124(4)
^{39}K	0.0433	0.0250	0.0683	0.071(2)
^{85}Rb	0.3024	0 2339	0.5363	0.546(12)
^{87}Rb	0.6808	0.5286	1.2094	1.23(3)
^{133}Cs	1.4437	0.7865	2.2302	2.25(5)

[a] See Ref. 4.

with those of earlier many-body diagrammatic calculations.[10,11] The contributions from the diagram 1(a), both in the present and earlier calculations[10,11] compare very well with each other for lithium and sodium and somewhat less closely for potassium, where the present value is about 15% larger than the earlier value from Ref. 11. In the case of the diagram 1(b), the present results are larger than the corresponding earlier results[10,11] for all three systems, the ratio of the former to the latter being 1.39, 1.25, and 1.16 for lithium, sodium, and potassium, respectively. One of the reasons for this difference is due to the fact that the amplitudes at the nucleus obtained from the unperturbed valence orbital wave functions[13] used here are 15% to 20% larger than those from the corresponding Hartree-Fock wave functions utilized in earlier many-body calculations. However, there is another contributing factor to this difference between the two results which we would like to point out. In order to evaluate the diagram 1(b) by the many-body perturbation procedure, one has to calculate the matrix elements of X for the complete set of basis functions. Among these matrix elements, those which connect continuum wave functions to continuum wave functions are difficult ones to handle in many-body perturbation procedures and are usually either estimated approximately[10] or neglected.[11] In the present investigation, this difficulty does not exist, since the perturbed wave functions are obtained by directly solving the requisite differential equations.[13,15]

As mentioned earlier in Sec. II, owing to the choice of unperturbed functions ϕ_{ns} utilized in this calculation and the use of the factor $f(r)$ in Eq. (7), some consistency and correlation effects beyond those associated with the diagrams in Fig. 1 are included in our results for k. We cannot therefore obtain quantitative estimates, from the difference between the theoretical and experimental values of k in Table I, of the consistency and correlation effects on k. However, the over-all very good agreement between theoretical and experimental k in Table I indicates that consistency and correlation effects beyond those associated with the hyperfine vertex are not of crucial importance for the alkali-metal atoms.

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