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Theory of negative fine and hyperfine structure in excited states of rubidium: $4\,^2D$ state

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The negative signs of the fine-structure constant and dipolar and contact hyperfine constants for the $4\,^2D$ state of the rubidium atom are all explained by the common mechanism of exchange polarization of core states by the valence $4d$ state. The results of the present one-electron theory for the fine-structure, dipolar, and contact hyperfine structure constants are -3.7 $(6.1-9.7)$ cm^{-1}, -0.37 $(0.29-0.65)\times 10^{24}$ cm^{-3}, and -2.1 $(0.0-2.1)\times 10^{24}$ cm^{-3}, respectively, where the values given in parentheses are, first, the (restricted) Hartree-Fock and, second, the exchange core-polarization contributions. By including the exchange core-polarization contribution, the resulting estimates are in reasonable accord with the corresponding observed values of these coupling constants: -0.176 cm^{-1}, -0.318×10^{24} cm^{-3}, and -4.22×10^{24} cm^{-3}, respectively. The possible importance of many-body and relativistic effects is discussed.

I. INTRODUCTION

The understanding of the properties of excited states of alkali-metal atoms has recently assumed major importance through the development[1,2] of very useful techniques for their study. Very interesting results have been obtained for the excited d states, in particular for the $4d\,^2D$ excited state of rubidium atom. In this system, experimental measurements have shown that the spin-orbit coupling constant[3,4] and the dipolar and contact hyperfine constants[4] are all negative in sign, while conventional restricted Hartree-Fock theory would give positive signs for the first two of these properties and a zero value for the contact hyperfine constant.

In the present work, we have demonstrated that for all three of these properties, a single mechanism, namely, the exchange polarization[5] of the core electron states by the valence electron, can in fact provide negative contributions which overcome the positive contributions from the valence electron for the spin-orbit coupling and dipolar hyperfine constants, while for the contact hyperfine constant this mechanism explains both the negative sign and finite magnitude of the observed experimental result.

Before proceeding to a quantitative analysis, a physical explanation of the origin of the negative sign of the three coupling constants can be given as follows: Considering first the spin-orbit coupling and dipolar hyperfine constants, the attractive exchange interaction between the valence $4d$ electron and core electrons such as the $4p$ type with spin parallel to the valence electron pulls the $4p$ parallel-spin electrons outwards, leading to a net relative increase of the density of antiparallel-spin $4p$ electrons in the inner region of the atom. This leads to indirect contributions to both the spin-orbit and dipolar hyperfine coupling constants of opposite sign to the direct contributions from the $4d$ electron, and can be of larger magnitude as a consequence of the relative proximity of the $4p$ electrons to the nucleus as compared to the $4d$ electron. If this happens, the indirect contributions can overpower the direct and determine the sign of the net coupling constants. This effect is reminiscent of the sizable nuclear quadrupole antishielding factors[6] for ions interacting with an external charge. A similar explanation applies for the negative sign of the exchange core polarization (ECP) contribution to the contact hyperfine coupling constant, with the $4s$ electron taking the role that the $4p$ electrons had in the previous situations. In the case of contact interaction there is no zero-order contribution from the $4d$ valence electron, the lowest-order contribution coming from the ECP effect itself. This discussion of the ECP effect has focused on the role of the $4s$ and $4p$ shells, because they have the largest exchange interaction with the $4d$. Of course, the inner shells ($1s$, $2s$, $2p$, etc.) are also subject to the ECP effect and will be included in this work.

In Sec. II we present a description of the method of calculation. A discussion of the results and conclusions are given in Sec. III.

II. PROCEDURE OF CALCULATION

The procedure used in our work involves the calculation of the second-order energies having one order in the exchange interaction between the $4d$ and core electrons and one order in the appro-

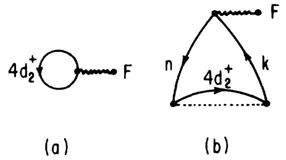

FIG. 1. (a) Direct and (b) ECP diagrams.

priate perturbation Hamiltonian. The latter is either the spin-orbit interaction, which couples the electron spin and orbital angular momenta via a function of the effective electric field, or the hyperfine coupling (contact or dipolar) between the electron spin and nuclear magnetic moment. In diagrammatic language,[7] these second-order energies are described by the diagram in Fig. 1(b), with Fig. 1(a) representing the direct zero-order contributions from the $4d$ state. In Fig. 1(b), the states n refer to occupied core states, while the states k represent excited states to which the core electron can be sent by any of the three perturbation Hamiltonians F, corresponding to the spin-orbit, dipolar hyperfine, and contact hyperfine interactions, represented by the interaction line at the top of the diagram. The bottom interaction line refers to the exchange interaction between the parallel-spin core and valence $4d$ electrons. The first-order energies [Fig. 1(a)] in the three cases are given by

$$\langle F\rangle_{4d}=\langle\psi_{4d}|F|\psi_{4d}\rangle\,, \tag{1}$$

while the second-order energies [Fig. 1(b)] are

$$\langle F\rangle_{\mathrm{ECP}}=-2\sum_{n,k}\frac{\langle\psi_n|F|\psi_k\rangle\langle\psi_k(1)\psi_{4d}(2)|(1/r_{12})|\psi_{4d}(1)\psi_n(2)\rangle}{\epsilon_n-\epsilon_k}\,. \tag{2}$$

For the three cases of spin-orbit, dipolar hyperfine, and contact hyperfine interactions, the perturbation Hamiltonian F is, respectively, given by

$$F_{\mathrm{SO}}=\frac{1}{r}\frac{dV}{dr}\,l_z s_z\,, \tag{3}$$

$$F_D=(1/r^3)\,P_2(\cos\theta)I_z s_z\,, \tag{4}$$

$$F_C=\delta(\vec{r})I_z s_z\,. \tag{5}$$

In Eqs. (3)–(5), multiplying factors involving products of a number of constants such as the nuclear magnetic moment, Bohr magneton, and Planck's constant have been dropped for the sake of brevity. They can be restored in making comparisons with experiment in terms of the appropriate units of measurement. For the dipolar and contact hyperfine constants, the multiplying factors are not necessary, because the experimental results are expressed in units of 10^{24} cm^{-3}. Also in Eq. (3), the potential V refers to a local approximation[8,9] of the Hartree-Fock potential and is obtained through the equation

$$V=\tfrac{1}{2}(\vec{\nabla}^2\psi/\psi)+\epsilon\,, \tag{6}$$

ϵ and ψ being the energy (in atomic units, e^2/a_0) and eigenfunction corresponding to the core state being investigated. Equation (3) is actually an approximation to the spin-orbit Hamiltonian and is adopted from considerations of practicability of calculation. The effects of this approximation and possible improvements will be discussed at the end of this article.

Equation (2) can of course be evaluated if the energy eigenvalues ϵ_k and ψ_k for the excited states are known. However, unless one is engaged in a full-scale many-body calculation,[7] this process is too time consuming to evaluate just $\langle F\rangle_{\mathrm{ECP}}$. Alternately, one can express $\langle F\rangle_{\mathrm{ECP}}$ in the form

$$\langle F\rangle_{\mathrm{ECP}}=-2\sum_n\left\langle\delta\psi_n(1)\psi_{4d}(2)\left|\frac{1}{r_{12}}\right|\psi_{4d}(1)\psi_n(2)\right\rangle\,, \tag{7}$$

where

$$\delta\psi_n=\sum_k\frac{\langle\psi_k|F|\psi_n\rangle\psi_k}{\epsilon_n-\epsilon_k} \tag{8}$$

represents the first-order perturbation of the core wave function ψ_n due to the perturbation Hamiltonian F. $\delta\psi_n$ can be obtained by solution of the first-order perturbation equation

$$(H_{0n}-\epsilon_n)\delta\psi_n=-(F-\langle\psi_n|F|\psi_n\rangle)\psi_n\,, \tag{9}$$

H_{0n} being the zero-order Hartree-Fock Hamiltonian for the core state ψ_n. The process of solution of Eq. (9) for the cases of contact and dipolar hyperfine interactions is explained extensively in the literature.[6,8,9] The process of solution for the case in which F refers to the spin-orbit operator in Eq. (3) is closely similar to that for the dipolar hyperfine interaction case. In this procedure, for the zero-order Hamiltonian H_{0n}, the sum of the kinetic energy $-\frac{1}{2}\vec{\nabla}^2$ and the potential energy V given by Eq. (6) is used. From the calculated $\langle F\rangle_{4d}$ and $\langle F\rangle_{\mathrm{ECP}}$, the corresponding direct and ECP contributions to the spin-orbit constant, in units of cm^{-1}, and to the dipolar and contact hyperfine interactions, in units of 10^{24} cm^{-3}, are given by

$$\zeta=\tfrac{1}{2}\alpha^2(e^2/a_0)(\langle F_{\mathrm{SO}}\rangle_{4d}+\langle F_{\mathrm{SO}}\rangle_{\mathrm{ECP}})\,, \tag{10}$$

$$\left\langle\frac{1}{r^3}\right\rangle_D=\frac{\langle F_D\rangle_{4d}+\langle F_D\rangle_{\mathrm{ECP}}}{\frac{1}{2}Ia_0^3\langle 4d_2|P_2(\cos\theta)|4d_2\rangle}\,, \tag{11}$$

$$\left\langle\frac{1}{r^3}\right\rangle_C=\frac{\langle F_C\rangle_{\mathrm{ECP}}}{\frac{4}{3}\pi a_0^3 I}\,, \tag{12}$$

TABLE I. List of various ECP contributions to the spin-orbit parameter ζ (in cm^{-1}) and dipolar and contact hyperfine constants $\langle 1/r^3\rangle_D$ and $\langle 1/r^3\rangle_C$ (in 10^{24} cm^{-3}).

Core orbitals	K	ζ	$\langle 1/r^3\rangle_D$	$\langle 1/r^3\rangle_C$
$3d$	0	0.743	0.028	
	2	0	0	
	4	0	0	
	Total	0.743	0.028	
$4p$	1	−13.837	−0.641	
	3	3.363	−0.067	
	Total	−10.474	−0.708	
$3p$	1	0.580	0.026	
	3	−0.109	0.002	
	Total	0.471	0.028	
$2p$	1	−0.623	−0.001	
	3	0.158	0	
	Total	−0.465	−0.001	
$4s$	2			−2.139
$3s$	2			0.103
$2s$	2			−0.078
$1s$	2			0
ECP total		−9.725	−0.653	−2.114

where α is the fine-structure constant. ζ, the spin-orbit constant in Eq. (10), is related to the fine-structure splitting frequency $\Delta\nu$ by the relation

$$\Delta\nu = \tfrac{5}{2}\zeta\,, \tag{13}$$

since $J=\frac{5}{2}$ for the $4d\,{}^2D_{5/2}$ state under investigation.

III. DISCUSSION OF RESULTS AND CONCLUSION

Using Eqs. (10)–(12) together with Eq. (7) for $\langle F\rangle_{\mathrm{ECP}}$ and the solutions $\delta\psi_n$ for the various core states from Eq. (9), we have evaluated various contributions to the spin-orbit, dipolar hyperfine, and contact hyperfine constants. These are listed in Table I. Since, in our present work, we are interested in strictly one-electron contributions, we have employed a one-electron Hartree-Fock self-consistent wave function for the $4d\,{}^2D$ configuration of rubidium, rather than using solutions from empirical potentials.[10]

First, consider the entries in Table I under spin-orbit coupling constant. The ECP contributions from the different core shells that can contribute, namely, $3d$, $4p$, $3p$, and $2p$, are listed separately. Also listed for each of these shells are the contributions from the multipole components K of $1/r_{12}$ in Eq. (7) and their sums. Since for spin-orbit interaction only the radial excitations $d\rightarrow d$ and $p\rightarrow p$ of the d and p core states are important, it follows that in Eq. (7) only $K=0,2,4$ contribute for the d core and $K=1,3$ contribute for the p cores. The cores which are entered in Table I for the dipolar hyperfine constant are the same as for the spin-orbit parameter. However, for this case, the angular excitations $p\rightarrow f$ and $s\rightarrow d$ can also contribute. Since the $4d$ orbital is rather external, one expects, from analogy with nuclear quadrupole antishielding calculations,[6] the angular contributions to have relatively minor importance. They have not been included in our present work. For the contact hyperfine interaction, only the s core states[5,9] contribute to the ECP effect, and it can be seen from Eq. (7) that only the $K=2$ term contributes in this case.

The important features of the ECP contributions are the following: First, for all three properties, the core states having $n=4$ make the leading contribution, the $4p$ being the important state for the spin-orbit coupling and dipolar hyperfine interacaction and $4s$ for the contact. This behavior is understandable, because the $4s$ and $4p$ cores exchange most strongly with $4d$. As regards the $3p$ and $2p$ contributions, it is interesting that for the spin-orbit coupling they are of comparable magnitude, while for the dipolar hyperfine case the $2p$ contribution is relatively negligible. This difference in behavior can be understood by realizing that the spin-orbit operator in Eq. (3) varies radially as $Z(r)/r^3$, while the dipole hyperfine Hamiltonian in Eq. (4) involves $1/r^3$, $Z(r)$ being the effective charge seen by the electron. Since $Z(r)$ increases rapidly as one approaches the nucleus (i.e., to the total nuclear charge Z for $r=0$), the increased spin-orbit coupling for the $2p$ state can effectively counterbalance the decrease in exchange with the $4d$ electron in going from $3p$ to $2p$. The $3d$ contributions to the spin-orbit coupling and spin-dipolar hyperfine interaction are comparable in magnitude to the $3p$ contributions. Actually the $3d$ contributions should be compared with the $4p$ contributions, because the radii of $3d$ and $4p$ orbitals are more nearly comparable than $3d$ and $3p$. The weaker results shown in Table I for $3d$ as compared to $4p$ are principally a consequence of the smaller amplitude near the nucleus of the $3d$ orbital due to the r dependence of the radial functions. For the contact hyperfine interaction, the $4s$ core state is the leading contributor and the $3s$ and $2s$ contributions are of comparable magnitude. The reason for the closer resemblance of $3s$ and $2s$ in contrast to the $3p$ and $2p$ contributions for dipolar hyperfine interaction, and closer to the spin-orbit case, is that the spin density for the

TABLE II. Summary of contributions and comparison with experiment.

	ζ (cm^{-1})	$\langle 1/r^3\rangle_D$ (10^{24} cm^{-3})	$\langle 1/r^3\rangle_C$ (10^{24} cm^{-3})
Direct	6.064	0.287	0.0
ECP	−9.725	−0.653	−2.114
Total	−3.661	−0.366	−2.114
Experiment	−0.176 [a]	−0.318 [b]	−4.22 [b]

[a] Reference 4(a).

[b] Reference 4(b).

contact hyperfine interaction increases more rapidly than $1/r^3$ as one approaches the nucleus, a behavior which is closer to that of $Z(r)/r^3$ in the spin-orbit case. Thus the variations in the ECP contributions in all three cases from the various shells can be understood from physical considerations.

The net coupling constants, which are the sum of the direct ($4d_2^+$) contribution and the total ECP contribution, are given in Table II, along with the experimental values.[4] First consider the spin-orbit coupling constant ζ. We see in Table II that the ECP contribution to the spin-orbit coupling is larger in magnitude than and of opposite sign to the direct contribution. Thus while the ECP contribution to ζ is qualitatively of the proper sign and magnitude and also shows how the negative fine-structure constant arises, the ECP effect by itself appears to be insufficient to explain the remaining difference with the experimental value. We have been led to this conclusion by corroborating the results for ζ in Table II, which were obtained by the methods described in Sec. II, with preliminary estimates obtained by many-body perturbation theory. Here we have used the same set of occupied Hartree-Fock atomic orbitals plus a complete set of virtual orbitals which are obtained as numerical solutions to appropriate one-electron equations. The conventional non-relativistic form of the spin–own-orbit and spin-other-orbit operators are taken.[11,12] That is, the spin–own-orbit operator is proportional to $l_z s_z/r^3$. We find that the direct contribution gives 5.29 cm^{-1}, which is composed of 9.19 cm^{-1} from the $4d$ spin–own-orbit operator and −3.91 cm^{-1} from the spin-other-orbit operator in the Hartree-Fock scheme.[11] This value, 5.29 cm^{-1}, compares reasonably well with the value 6.06 cm^{-1} which was obtained by employing Eqs. (1), (3), and (6) of Sec. II. The total ECP contribution to the spin–own-orbit operator obtained by many-body perturbation theory is −10.4 cm^{-1}, which again is reasonably close to the value, −9.73 cm^{-1}, obtained by the methods of Sec. II. The shellwise contributions to the ECP effect also agree well.

Having independently verified the estimates of the spin-orbit coupling constant presented in Tables I and II, we are left to consider the remaining difference between estimated and experimental coupling constants. There are two possible effects which come to mind. The first is electronic correlation, which requires higher-order perturbation theory and a more systematic way of incorporating those effects, and which we would expect to be an important effect here. Secondly, in order to properly handle many-electron effects, the proper nonrelativistic form[11] of the spin-orbit Hamiltonian (i.e., the one composed of one- and two-body operators derived[12] by a Foldy-Wouthuysen transformation of the many-electron Dirac Hamiltonian) must be used. Thus the form of the Hamiltonian chosen in Eq. (3) is suitable for single-particle excitation effects, as in this work, but it is not appropriate for the inclusion of many-particle effects. Therefore the program for improving agreement with experiment is to use the proper nonrelativistic spin-orbit Hamiltonian and include the influence of correlation effects. Alternatively, a relativistic many-body treatment of the atom would avoid the need for using an approximate spin-orbit Hamiltonian.

For the dipolar and contact hyperfine constants the results in Table II show that the ECP contribution gives a substantial improvement in the Hartree-Fock estimates and explains the origin of the negative sign of both constants. The contact hyperfine constant, which up to the order considered here arises entirely from the ECP effect, is about one-half the size determined experimentally.[4] The difference between theory and experiment is most likely due to correlation effects. There can be two types of correlation effects that can contribute to the contact hyperfine interaction. First, the valence d electron itself, by pair correlation[7] with any of the core electrons, can pick up some s character and contribute to the spin density at the nucleus. Second, the changes in the radial and angular characters of the valence electron can alter its exchange interaction with the core s states.

The dipolar hyperfine constant appears to be in reasonable agreement with experiment after inclusion of the ECP contribution. However, we have omitted the angular polarization contributions to the dipolar interactions which arise when core p shells are excited into virtual f states by an exchange interaction with valence $4d$ electrons. Similarly, polarizations of the type $3d\rightarrow s$, $3d\rightarrow g$, and $ns\rightarrow d$ are also possible. Nevertheless, as remarked earlier, these angular polarization effects may not be very important in the present case, as has been the usual result for other systems investigated.[7,8] Correlation is expected to have an influence on the dipolar interaction, since, as with the other properties, the 4*d* electron is fairly loosely bound and can therefore be deformed appreciably by pair correlation, especially with the 4*s*- and 4*p*-shell electrons.

In conclusion, the present work on the $4\,^2D$ state of rubidium clearly demonstrates that the exchange core polarization effect is of crucial importance for explaining the origin of the observed signs and to varying degrees the magnitudes of the spin-orbit as well as hyperfine coupling constants. The same mechanism should be considered for explanation of similar data on other excited *d* states of rubidium and other alkali atoms. For a complete quantitative explanation of these properties our work indicates that a thorough and detailed treatment of correlation effects has to be carried out.

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