

# Tensor polarizability of the ground state of alkali atom

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## Ground state wave function in external field

At this stage we neglect hfs and write ground state wave function in electric field  $\mathbf{E} = E\hat{z}$ :

$$\Psi_m = C_s |s_{1/2}m\rangle + \frac{\langle p_{1/2}m | r_z E | s_{1/2}m \rangle}{E_{sp}} |p_{1/2}m\rangle + \frac{\langle p_{3/2}m | r_z E | s_{1/2}m \rangle}{E_{sp}} |p_{3/2}m\rangle, \quad (1)$$

where  $C_s$  is normalization coefficient and

$$\langle p_j m | r_0 | s_{1/2} m \rangle = (-1)^{3/2-m} \begin{pmatrix} j & 1 & 1/2 \\ -m & 0 & m \end{pmatrix} \sqrt{\frac{2j+1}{3}} R_{sp}. \quad (2)$$

If we introduce coefficients

$$C_j = \sqrt{j+1/2} \frac{R_{sp} E}{3E_{sp}}, \quad (3)$$

then wave function (1) assumes the form of a molecular  $\sigma$ -orbital:

$$\Psi_m = C_s |s_{1/2}m\rangle - (2m)C_{1/2} |p_{1/2}m\rangle + C_{3/2} |p_{3/2}m\rangle, \quad (4)$$

where

$$C_s = \left(1 - C_{1/2}^2 - C_{3/2}^2\right)^{1/2}. \quad (5)$$

Convenience of Eq. (4) is that we can use results obtained for diatomic molecules in [1].

## Contribution of magnetic hfs to polarizability

Coefficients in Eq. (4) depend on the electric field and so do the hyperfine matrix elements calculated with this wave function. The field dependent part of the hyperfine structure corresponds to the hyperfine correction to the polarizability of the ground state. This correction includes isotropic and dipole terms, which contribute to scalar and tensor polarizabilities correspondingly.

Operator of the magnetic hfs for the wave function (4) has the following form:

$$H_{\text{hf}}^m = A_{\text{iso}} \mathbf{I} \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} \mathbf{s} + A_{\text{dip}} \mathbf{I} \begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix} \mathbf{s}, \quad (6)$$

where  $\mathbf{s}$  is an effective spin,  $s = 1/2$ . Constants  $A_{\text{iso}}$  and  $A_{\text{dip}}$  were calculated in [1]:

$$\delta A_{\text{iso}} = - \left( C_{1/2}^2 + C_{3/2}^2 \right) A_s + \frac{4}{9} C_{1/2}^2 h_{11} + \frac{8\sqrt{2}}{9} C_{1/2} C_{3/2} h_{13} + \frac{8}{9} C_{3/2}^2 h_{33}, \quad (7)$$

$$A_{\text{dip}} = -\frac{8}{9} C_{1/2}^2 h_{11} + \frac{2\sqrt{2}}{9} C_{1/2} C_{3/2} h_{13} - \frac{8}{45} C_{3/2}^2 h_{33}, \quad (8)$$

where we used (5) and omitted field independent part of isotropic constant  $A_{\text{iso}}$ , which is equal to  $A_s$ . The radial integrals of the hyperfine operator  $h_{jj}$  can be expressed in terms of the atomic hyperfine constants of the corresponding  $p_j$ -level:

$$h_{11} = -\frac{3}{4} A_{p_{1/2}}, \quad h_{33} = \frac{15}{8} A_{p_{3/2}}. \quad (9)$$

The nondiagonal radial integral  $h_{13}$  does not contribute to atomic hfs and, therefore, can not be linked directly to any experimentally measured quantity. However, in the one-particle nonrelativistic approximation all three radial integrals are related to each other:

$$4h_{13} = -2h_{33} = h_{11}. \quad (10)$$

The nondiagonal contribution to both  $A_{\text{iso}}$  and  $A_{\text{dip}}$  is numerically small and we can use Eq. (10) to link  $h_{13}$  to either  $A_{p_{1/2}}$  or  $A_{p_{3/2}}$  without introducing significant error. Below we will use relation  $h_{13} = -\frac{15}{16}A_{3/2}$  to keep closer to [2]. Note, that Eqs. (9) and (10) imply that

$$A_{p_{1/2}} = 5A_{p_{3/2}}, \quad (11)$$

which can be tested experimentally.

Eqs. (7) – (10) yield

$$\delta A_{\text{iso}} = -\left(C_{1/2}^2 + C_{3/2}^2\right) A_s - \frac{1}{3}C_{1/2}^2 A_{p_{1/2}} - \frac{5\sqrt{2}}{6}C_{1/2}C_{3/2}A_{p_{3/2}} + \frac{5}{3}C_{3/2}^2 A_{p_{3/2}}, \quad (12)$$

$$A_{\text{dip}} = \frac{2}{3}C_{1/2}^2 A_{p_{1/2}} - \frac{5\sqrt{2}}{24}C_{1/2}C_{3/2}A_{p_{3/2}} - \frac{1}{3}C_{3/2}^2 A_{p_{3/2}}. \quad (13)$$

These equations can be simplified if we use explicit form of coefficients  $C_j$  (3):

$$\delta A_{\text{iso}} = -\frac{1}{27}\left(\frac{R_{sp}E}{E_{sp}}\right)^2 (9A_s + A_{p_{1/2}} - 5A_{p_{3/2}}), \quad (14)$$

$$A_{\text{dip}} = \frac{1}{108}\left(\frac{R_{sp}E}{E_{sp}}\right)^2 (8A_{p_{1/2}} - 13A_{p_{3/2}}). \quad (15)$$

Further simplification takes place in the one-particle nonrelativistic approximation (11):

$$\delta A_{\text{iso}} \approx -\frac{1}{3}\left(\frac{R_{sp}E}{E_{sp}}\right)^2 A_s, \quad (16)$$

$$A_{\text{dip}} \approx \frac{1}{4}\left(\frac{R_{sp}E}{E_{sp}}\right)^2 A_{p_{3/2}}. \quad (17)$$

Note, that relation (11) between  $A_{p_{1/2}}$  and  $A_{p_{3/2}}$  does not hold even for some light atoms because of the core polarization effects. The most striking example is Li, where core polarization changes the sign of the constant  $A_{p_{3/2}}$ .

### 1. Scalar polarizability.

Constant  $\delta A_{\text{iso}}$  contributes to the Stark shift of the transition  $F = I - 1/2, M \rightarrow F' = I + 1/2, M$ :

$$\delta\nu_{\text{iso}}(\Delta F = 1) = \delta A_{\text{iso}}(2I + 1). \quad (18)$$

The contribution of the ground state hyperfine constant  $A_s$  dominates here and approximate expression (16) should work quite good.

### 2. Tensor polarizability.

Dipole part of the hyperfine interaction  $A_{\text{dip}}$  results in the quadrupole splitting of the hyperfine levels. Corresponding part of the effective hyperfine operator (6) has the form:

$$H_{\text{dip}} = \sqrt{6}(I \otimes s)_0^2 A_{\text{dip}}. \quad (19)$$

Spherical tensor technique immediately allows to calculate expectation value of this operator for the state  $|F, M\rangle$ :

$$\langle F, M | H_{\text{dip}} | F, M \rangle = (-1)^{F-M} 3(2F + 1) \sqrt{5I(I+1)(2I+1)} \begin{pmatrix} F & 2 & F \\ -M & 0 & M \end{pmatrix} \left\{ \begin{matrix} I & I & 1 \\ 1/2 & 1/2 & 1 \\ F & F & 2 \end{matrix} \right\} A_{\text{dip}}. \quad (20)$$

Note, that  $A_{\text{dip}} \sim E^2$  and, therefore, Eq. (20) gives us tensor polarizability of the ground state. It obviously gives rise to the Stark shifts for hfs transitions with  $\Delta F = 0, \Delta M = 1$  as well as for transitions with  $\Delta F = 1$ , though the

latter is dominated by (18). As we mentioned above, an approximate expression (17) for the  $A_{\text{dip}}$  should be used with caution. It is most accurate for Na and holds within 20% accuracy for K, Rb and Cs, but completely fails for Li and Fr. On the contrary, expression (15) relies on the relations (10) only for nondiagonal term, which account for about 20% of the answer, and should be reasonably accurate for all alkalis.

The operator (19) has nondiagonal in  $F$  matrix elements. That corresponds to the fact that in the external electric field  $F$  is not an exact quantum number. However, corresponding mixing is extremely small:

$$\frac{\langle F = I + 1/2, M | H_{\text{hf}} | F = I - 1/2, M \rangle}{E_{F=I+1/2} - E_{F=I-1/2}} \sim \frac{A_{\text{dip}}}{A_s} \sim \left( \frac{R_{sp} E}{E_{sp}} \right)^2 \frac{A_{p_{3/2}}}{A_s} \quad (21)$$

and  $F$  is, in fact, a good quantum number.

### Contribution of electric quadrupole hfs to polarizability

Electric quadrupole hfs for the wave function (4) is described by the following operator [3]:

$$H_{\text{hf}}^e = \frac{-q_0 Q}{8I(2I-1)} (3I_z^2 - I(I+1)), \quad (22)$$

where  $Q$  is the quadrupole moment of the nucleus and electronic matrix element  $q_0$  is:

$$q_0 = \frac{8\sqrt{2}}{5} C_{1/2} C_{3/2} R_{13} + \frac{4}{5} C_{3/2}^2 R_{33}. \quad (23)$$

Radial integral  $R_{33}$  is connected to the quadrupole constant of the  $p_{3/2}$ -level as follows

$$QR_{33} = \frac{5}{2} B_{p_{3/2}}, \quad (24)$$

and assuming  $R_{13} \approx R_{33}$ , which holds in one-particle nonrelativistic approximation, we arrive at

$$q_0 Q = \left( 4\sqrt{2} C_{1/2} C_{3/2} + 2C_{3/2}^2 \right) B_{p_{3/2}} = \frac{4}{3} \left( \frac{R_{sp} E}{E_{sp}} \right)^2 B_{p_{3/2}}. \quad (25)$$

Note, that here nondiagonal term is much more important (it accounts for  $\frac{2}{3}$  of the answer!) than for magnetic hfs contribution and, therefore, this expression is less accurate than (15). Fortunately, electric quadrupole contribution is significantly smaller, than magnetic one for all alkalis with exception of Fr.

Calculation of the matrix element of the operator (22) is quite straightforward, the answer being:

$$\langle F, M | H_{\text{hf}}^e | F, M \rangle = \frac{2(3M^2 - F(F+1))(4I(I+1)F(F+1) - 3X(X+1))}{9I(2I-1)(2F-1)2F(2F+2)(2F+3)} \left( \frac{R_{sp} E}{E_{sp}} \right)^2 B_{p_{3/2}}, \quad (26)$$

where  $X = \frac{3}{4} - I(I+1) - F(F+1)$ .

Obviously, the matrix element (26) contributes directly to the tensor polarizability of the ground state. The final answer for the latter is given by the sum of Eqs. (20) and (26).

### Comparison with Sandars

In 1967 Sandars made very similar calculations of the Stark shifts for the hyperfine transitions of alkalis. There are two minor differences between two approaches. First, Sandars used nonrelativistic operators for the hyperfine interaction, which corresponds to our Eqs. (16) and (17). As we mentioned above, this approximation is not always good. Second, we use experimental data for the radial integrals  $R_{sp}$ , while Sandars used data for scalar polarizability  $\alpha$ . In both approaches it is supposed that dominant contribution comes from the lowest  $p$ -shell, therefore there is one-to-one correspondence between  $\alpha$  and  $R_{sp}^2$ :

$$\alpha = \frac{2R_{sp}^2}{3E_{sp}}. \quad (27)$$

Still, the accuracy, with which these quantities are known from the experiment, can differ significantly. Also, when radial integrals  $R_{sp}$  are used, it is easier to introduce different corrections. In particular, one can account for the difference between  $R_{sp_{1/2}}$  and  $R_{sp_{3/2}}$  as well as account for the higher  $p$ -shells.

With these substitutions our results should correspond to those of Sandars. In fact there is such an agreement for the hyperfine level  $F = I + 1/2$ , while for the level  $F = I - 1/2$  our Eq. (20) gives the opposite sign of the shift, in comparison with expression of Sandars. Eq. (26) differs from corresponding expression of Sandars by the factor  $\frac{2}{3}$ .

## Numerical results for Stark shifts in the hfs transitions

The above expressions allow to calculate Stark shifts for the transitions between the hyperfine levels of the ground state of alkalis. All the relevant constants are known from the experiment and listed in the Table.

		<sup>7</sup> Li	<sup>23</sup> Na	<sup>39</sup> K	<sup>85</sup> Rb	<sup>133</sup> Cs	<sup>221</sup> Fr
$I$		$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{5}{2}$
$\Delta_{sp}$	(cm <sup>-1</sup> )	14904	16965	13014	12698	11456	13081
$\Delta_{so,n_0p}$	(cm <sup>-1</sup> )	0.34	17.2	57.9	238	554	1687
$A_{n_0s}$	(GHz)	0.402	0.886	0.231	1.01	2.30	6.21
$A_{n_0p_{1/2}}$	(MHz)	45.9	94.3	27.8	120.7	292	811
$A_{n_0p_{3/2}}$	(MHz)	-3.06	18.7	6.1	25.0	50.3	66.5
$B_{n_0p_{3/2}}$	(MHz)	-0.2	2.9	2.8	26.0	-0.4	-260
$R_{n_0s,n_0p}$	(a.u.)	4.05	4.29	5.06	5.03	5.50	5.11
Stark shift for transition $I + 1/2, I + 1/2 \rightarrow I + 1/2, I - 1/2$							
this work	(10 <sup>-10</sup> Hz/(V/cm) <sup>2</sup> )	-11.5	-11.6	-7.5	-30.0	-172	-482
theor. [2,4]	(10 <sup>-10</sup> Hz/(V/cm) <sup>2</sup> )	—	-13	-7	-39	-155	—
exper. [4]	(10 <sup>-10</sup> Hz/(V/cm) <sup>2</sup> )	—	-11.18	-4.8	-22.8	-137.2	—
Stark shift for transition $I - 1/2, 0 \rightarrow I + 1/2, 0$							
this work	(10 <sup>-6</sup> Hz/(V/cm) <sup>2</sup> )	-0.072	-0.136	-0.084	-0.57	-2.55	-3.44
theor. [2,4]	(10 <sup>-6</sup> Hz/(V/cm) <sup>2</sup> )	—	-0.141	-0.089	-0.64	-2.82	—
exper. [5]	(10 <sup>-6</sup> Hz/(V/cm) <sup>2</sup> )	—	—	—	—	-2.271	—

Experimental measurements of the Stark shifts were performed for transitions  $F = I + 1/2, M = I + 1/2 \rightarrow F = I + 1/2, M' = I - 1/2$  [4] and  $F = I + 1/2, M = 0 \rightarrow F' = I - 1/2, M = 0$  [5]. Theoretical and experimental results for these transitions are also listed in the Table. For the transition of the second type we neglected tensor contribution and used Eq. (18) to calculate the shift. To compare our results to those of Sandars, we calculated corresponding shifts using his expressions and polarizabilities from [4].

It is seen from the Table, that discrepancy between theory and experiment is not small. Na is the only atom, where agreement is good. It may be not a simple coincidence that it is also the only atom, where Eq. (11) holds. As we mentioned above, this relation requires both nonrelativistic and one-particle approximation to hold. Therefore, we can conclude that many-body corrections for Na are smaller, than for other light atoms. That can indicate that the accuracy of the theory is limited by the one-particle approximation, which was used in both calculations.

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