Frequency Shifts in Hyperfine Splitting of Alkalis: a Correction*

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The effect of the deformation of the wave functions by Van der Waals interactions, previously ignored, upon the hyperfine shifts of alkalis caused by rare gas atoms is computed. It is found to be large and clearly in need of consideration. When applied to the experimentally observed shifts, the model proposed earlier, with the new values of the interaction constants, leads to "interaction radii" somewhat greater than before and more nearly equal to gas kinetic radii.

AFTER the appearance of an article[1] by the title above, Adrian published a calculation[2] which led to a formula for the differential Van der Waals forces between a hydrogen atom in its separate hyperfine states and a perturbing atom, quite different from the one computed in reference 1 for alkalis. Adrian's result is

$$\Delta E(\text{hyperfine}) = \mathscr{E}[1/(\bar{E}+I_2)+2/\bar{E}]\Delta E(\text{dispersion}). \quad (1)$$

Here $\Delta E(\text{hyperfine})$ is the hyperfine energy shift, $\mathscr{E}$ is the unperturbed hyperfine energy, $\bar{E}$ is an "average" energy of the H atom (taken to be the average of the resonance P-state energy and the ionization energy relative to the ground state), I_2 is the ionization energy of the perturber (in the cases of interest a noble gas atom), and $\Delta E(\text{dispersion})$ is the Van der Waals dispersion energy (a negative quantity). In I the second term in the brackets in Eq. (1) is missing.

If Adrian's result is applied to the alkalis, his predicted $\Delta E(\text{hyperfine})$ is as much as 5 to 10 times that of I; for hydrogen the predictions differ by a factor ~ 3. This has caused us to reconsider the problem and to look for the source of the discrepancy. We shall show that the added term in (1) is indeed present, even though it is overestimated when computed by that formula.

Physically, the added term arises from the deformation of the wave function by the hyperfine interaction[3] itself, which was neglected in I. It disappeared from the mathematics of that paper in its later stages through an approximation which equated the f values for the higher and lower hyperfine states of the alkali atom. When this approximation is avoided, terms like those in question, but with a somewhat different meaning of $\bar{E}$, come into evidence.

The correct result may be obtained from Eqs. (5) and (19) of I. We take as the starting point of our

discussion Eq. (19) of I.

$$(p'|V|p)^2 = \frac{4e^4}{9R^6}\sum_{M=-1}^{1}\left\{\frac{[3(2j_1+1)(2J'+1)(2J+1)]^{\frac{1}{2}}}{(1-M)!(1+M)!}\right.$$

$$\times C(j_11j_1'; m_1M)W(Jj_1J'j_1'; I1)W(0J1J'; S1)\Bigg\}^2$$

$$\times (L'|r_1|L)^2(j_2'|r_2|j_2)^2. \quad (2)$$

In the case of cesium, for which the derivation was carried out explicitly, the hyperfine quantum number $j_1=4$ in connection with the matrix elements $(p'|V|p)$ appearing in Eq. (5) of I; for $(q'|V|q)$, $j_1=3$. The dependence on j_1 in all factors of (2) is indicated, except in the radial matrix elements $(L'|r_1|L)$ and $(j_2'|r_2|j_2)$. The latter matrix element, which refers to the noble gas atom, needs no further attention, but $(L'|r_1|L)$ must be more closely examined. With a fuller display of quantum numbers, this radial matrix element reads

$$(n'L'j_1'|r_1|nLj_1),$$

which is meaningful for the one-electron system to which the present theory applies. The present theory is limited to the ground state of alkali atoms; hence $L=0$, $L'=1$, and the hyperfine quantum number $j_1'=j_1$ (which is either 3 or 4); n labels the ground state and n' the various excited states.

First, we evaluate the difference

$$(n'14|r_1|n04)-(n'13|r_1|n03)\equiv\Delta(n,n'). \quad (3)$$

To do this, we expand the function ψ_{n0j_1} by perturbation theory using the hyperfine operator $\mathcal{3C}$ as the perturbation. Note is taken of the fact that in making the expansion, matrix elements diagonal in L and J are large compared with nondiagonal elements. We may therefore use the hyperfine operator for S states[4]:

$$\mathcal{3C}=\text{const}\times\delta(\mathbf{r}_1,0)\mathbf{I}\cdot\mathbf{S}.$$

To obtain terms of the same form as Adrian's, we neglect the perturbation in $\psi_{n'1j_1}$, which yields almost no net contribution to $\Delta E(\text{hyperfine})$. One therefore

[1] H. Margenau, P. Fontana, and L. Klein, Phys. Rev. 115, 87 (1959); referred to as I.

[2] F. Adrian, J. Chem. Phys. 32, 972 (1960).

[3] This is in complete accord with a comment made by Dr. P. Bender at the Ann Arbor Conference on Optical Pumping, University of Michigan, June, 1959, (unpublished), of which the present authors were not aware.

[4] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).

finds

$$\Delta(n,n') = \sum_{n''}{}' \frac{(n04|\mathfrak{K}|n''04) - (n03|\mathfrak{K}|n''03)}{E_n - E_{n''}}$$
$$\times (n''0|r|n'1). \quad (4)$$

According to Eq. (5) of I, the hyperfine energy difference is given by

$$\Delta E_{(\text{hyp})} = \sum_{p'}{}' \frac{(p'|V|p)^2}{E_p - E_{p'}}$$
$$- \sum_{p'}{}' \frac{(p'|V|p)^2}{E_p - E_{p'}} \frac{(n'13|r_1|n03)^2}{\mathcal{E}(n'14|r_1|n04)^2},$$

where now every $(p'|V|p)$ refers to states $j_1=4$. Hence, by the arguments of I ($\bar{E}$ here is the resonance energy of the alkali atom),

$$\Delta E_{(\text{hyp})} \cong \frac{\mathcal{E}\Delta E_{(\text{disp.})}}{\bar{E}+I_2} + \sum_{p'}{}' \frac{(p'|V|p)^2}{E_p - E_{p'}}$$
$$\times \left\{ 1 - \frac{(n'13|r_1|n03)^2}{(n'14|r_1|n04)^2} \right\}, \quad (5)$$

and the bracket, by virtue of the near equality of the two r_1 elements, becomes

$$2\Delta(n,n')/(n'14|r_1|n04).$$

Hence the second term of Eq. (5) reads

$$S = 2 \sum_{p'}{}' \frac{(p'|V|p)^2}{E_p - E_{p'}} \frac{\Delta(n,n')}{(n'14|r_1|n04)}.$$

Now as is seen from Eq. (1) of this paper, $(p'|V|p)^2$ contains the factor $(n'14|r_1|n04)^2$; hence S receives its largest contributions from terms in which $n'=n$. The differences $E_p - E_{p'}$ which correspond to the elements $(p'|V|p)$ are dominated by the excited state energies of the rare gas atom. We may therefore write

$$S \cong 2 \sum_{p'}{}' \left[\frac{(p'|V|p)^2}{(n'14|r_1|n04)^2} \frac{1}{(E_p - E_{p'})_{n'=n}} \right]$$
$$\times (n'14|r_1|n04)\Delta(n,n'), \quad (6)$$

where now the contents of the bracket depend on all quantum numbers indicated by p' except n'. We notice also that in the expression for $\Delta E(\text{dispersion})$,

$$\sum_{p'}{}' \frac{(p'|V|p)^2}{(E_p - E_{p'})},$$

only those terms for which $n'=n$ are large. As before, we may split the summation on p' into its n'-dependent

and n'-independent parts,

$$\Delta E(\text{dispersion}) \cong \sum_{p'}{}' \left[\frac{(p'|V|p)^2}{(n'14|r_1|n04)^2} \times \frac{1}{(E - E_p)_{n'=n}} \right]$$
$$\times (n'14|r_1|n04)^2, \quad (7)$$

where the contents of the bracket are independent of n'. Performing the summation over n', we obtain

$$\Delta E(\text{dispersion}) \cong \sum_{p'}{}' \left[\frac{(p'|V|p)^2}{(n'14|r_1|n04)^2} \frac{1}{(E_p - E_{p'})_{n'=n}} \right]$$
$$\times (n04|r_1^2|n04). \quad (8)$$

Substituting this result into (6) yields

$$S \cong \frac{2\Delta E(\text{dispersion})}{(n04|r_1^2|n04)} \sum_{n'} (n'14|r_1|n04)\Delta(n,n'). \quad (9)$$

Here we insert Eq. (4) and perform the summation over n', obtaining

$$S = \frac{2\Delta E(\text{dispersion})}{(n0|r_1^2|n0)}$$
$$\times \sum_{n''}{}' \frac{(n04|\mathfrak{K}|n''04) - (n03|\mathfrak{K}|n''03)}{(E_n - E_{n''})}$$
$$\times (n''0|r_1^2|n0). \quad (10)$$

To evaluate this summation for the alkalis we use hydrogenlike functions with an effective nuclear charge Z. Furthermore we take the unperturbed hyperfine splitting energy to be proportional to the charge density at the nucleus:

$$\mathcal{E} = (n04|\mathfrak{K}|n04) - (n03|\mathfrak{K}|n03) \propto \psi_n^2(0),$$

and

$$(n04|\mathfrak{K}|n''04) - (n03|\mathfrak{K}|n''03)$$
$$= \mathcal{E}\psi_{n''}(0)/\psi_n(0) = \mathcal{E}(n/n'')^{\frac{3}{2}}.$$

The elements $(n''0|r_1^2|n0)$, in which we now neglect the dependence on j_1, are evaluated by using formulas derived for another purpose by Fontana[5]:

$$(n''0|r_1^2|n0) = 4\frac{a_0^2}{Z^2} \left(\frac{1}{nn''} \right)^{\frac{3}{2}} (n-1)!(n''-1)! \left(\frac{nn''}{n+n''} \right)^5$$
$$\times \sum_{\xi,\eta=0} \frac{(-1)^{\xi+\eta}(4+\xi+\eta)!}{(n''-\xi-1)!(n-\eta-1)!(\eta+1)!(\xi+1)!\eta!\xi!}$$
$$\times \left(\frac{2n}{n+n''} \right)^\xi \left(\frac{2n''}{n+n''} \right)^\eta,$$

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[5] P. Fontana, Ph.D. thesis, Yale University, 1960 (to be published).

and, if $n=n''$, this equation reduces to

$$(n0|r_1{}^2|n0)=\frac{9}{2Z^2}a_0{}^2\sum_{\xi=0}\frac{(4+\xi)!}{(n-\xi-1)!^2(4+\xi-n)!^2\xi!}.$$

All terms containing the factorial of a negative integer in the denominator vanish. Energies are represented by

$$E_n=-\mathrm{Ry}Z^2/n^2,$$

the values of Z for the groundstates of the different alkalis being 1.84, 2.26, 2.77, and 3.21 for Na, K, Rb, and Cs.

In the actual calculation, matrix elements were computed explicitly for low values of n''; for higher elements a sum rule was employed. It is necessary, of course, to include in the summation the inner levels of the alkali atom even though they are occupied.

The one-electron picture with the same Z for all states was consistently maintained throughout the calculation, as is required for the sake of perturbation theory. To test the sensitivity of the result, we have also computed S with an assignment of different Z_n to different states, thus destroying the orthogonality of the states; the Z_n were taken from spectroscopy (with extrapolation for occupied states). This procedure yielded the same results for Na within a few percent.

If the results are written in the form

$$S=(2c/I_1)\mathscr{S}\Delta E(\text{dispersion}),\qquad(11)$$

where I_1 is again the ionization potential of the alkali, then the values of c are 1.1 for hydrogen, 1.0 for sodium, and 1.1 for cesium. This seems to suggest that, with

TABLE I. Values of the constant a, appearing in the formula $\Delta E(\text{hyperfine})=-a/R^6$.

Gas	$a(\text{Cs}^{133})$	$a(\text{Rb}^{87})$
He	24.55×10^{-5}	15.40×10^{-5}
Ne	46.60×10^{-5}	29.30×10^{-5}
N_2	213.3×10^{-5}	134.1×10^{-5}
Ar	198.6×10^{-5}	125.1×10^{-5}
Kr	303.3×10^{-5}	190.4×10^{-5}
Xe	498.0×10^{-5}	

TABLE II. Comparison of d and ϵ for Cs-noble gas interactions.

Interaction	d	ϵ
Cs—He	3.58	0.60
Cs—Ne	3.75	0.70
Cs—N_2	4.24	0.50
Cs—Ar	4.07	0.85
Cs—Kr	4.18	0.96
Cs—Xe	4.27	1

sufficient accuracy, c can be taken to be 1 for the cases in which we are interested.

The complete formula for the shift induced by a rare gas atom in the hyperfine energy of an alkali thus reads, approximately,

$$\Delta E(\text{hyperfine})=\Delta E(\text{dispersion})\left(\frac{1}{\bar{E}+I_2}+\frac{2}{I_1}\right)\mathscr{S},\quad(12)$$

where again I_1 and I_2 are the ionization energies of the alkali atom and the rare gas atom, and $\bar{E}$ is the resonance energy of the alkali.

The constant $a=-R^6\Delta E(\text{hyperfine})$ is considerably altered from the values given in I, as is seen in Table I. The relative magnitudes of the coefficients remain about the same, and for this reason the effect of the change upon the line shifts we wish ultimately to compute is not very great.

We employ the same reasoning as in I [see formulas (29) and (30)] and the same notation: d is the distance at which the "attractive" interaction changes to a "repulsive" one in analogy with ordinary intermolecular forces; ϵ is a measure of the steepness of the "repulsive" interaction. The results are given in Table II. The parameter ϵ has the same trend as before, and d is now, curiously, in even better accord with kinetic theory radii.

More refined calculations of the shifts, with special attention to their temperature dependence, were performed by Robinson[6] on the basis of the numerical values given in I. Simple arguments lead us to believe that his results remain substantially unchanged when the new interaction constants are employed, except for slight changes in parameters as in Table II.

[6] L. B. Robinson, Phys. Rev. 117, 1275 (1960).