# New Term in Atomic Zeeman Energy

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An unexpected Zeeman shift discovered in recent measurements of ground-state rubidium hyperfine structure in strong magnetic fields can be explained as an effect of the hyperfine interaction in the mixing of electronic states of different principal quantum number and spin direction into the ground state. A term of the form $\beta m_I^2 m_J B/J$ is induced in the ground-state energy. A calculation based on the Fermi-Segrè treatment of alkali-metal atoms yields the theoretical values $\beta(^{85}\mathrm{Rb})=0.016$ Hz/T and $\beta(^{87}\mathrm{Rb})=0.18$ Hz/T, which are in good agreement with the experimental results $\beta(^{85}\mathrm{Rb})=0.0162(14)$ Hz/T and $\beta(^{87}\mathrm{Rb})=0.168(15)$ Hz/T.

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Fletcher, Lipson, and Larson[1] have carried out highly precise measurements of the hyperfine structure and Zeeman shifts in ground-state rubidium atoms in strong magnetic fields. They report an interesting and as yet unexplained shift in the Zeeman levels that is consistent with a field-dependent change in $g_I/g_J$, and nuclear to electronic $g$-factor ratio. Alternatively, as they point out, their results are equally consistent with the existence of an additional term of the form $\beta m_I^2 m_J B/J$ in the ground-state energy. In the latter case, the experimental results imply that $\beta(^{85}\mathrm{Rb})=0.0162(14)$ Hz/T, and $\beta(^{87}\mathrm{Rb})=0.168(15)$ Hz/T, which scale as $g_I^2$ for the two isotopes.

Here I show that an $m_I^2 m_J B$ term is indeed induced in the Zeeman energy by the magnetic dipole hyperfine interaction, through coupling of higher electronic levels (with flipped electron spin) into the ground state. This term should be of order $\mu_B B(E_{\mathrm{hfs}})^2/(E_{\mathrm{atom}})^2$, which is about the right size, and it should scale as $g_I^2$ in agreement with experiment. A calculation of this term using the Fermi-Segrè treatment of alkali-metal atoms is outlined below, and yields values of $\beta$ for each Rb isotope in good agreement with the measurements.

I begin with the relevant part of the Hamiltonian giving the magnetic interaction of the nucleus and valence electron:

$$H_m=H_B+H_{\mathrm{hfs}},\quad H_B=\mu_B(g_J\mathbf{J}-g_I\mathbf{I})\cdot\mathbf{B},\quad H_{\mathrm{hfs}}=\tfrac{8}{3}\pi\mu_B^2 g_I g_J\delta(\mathbf{r})\mathbf{I}\cdot\mathbf{J}+2\mu_B^2 g_I[\nabla(\mathbf{I}\cdot\mathbf{r}/r^3)]\cdot(\mathbf{L}-\mathbf{S}). \tag{1}$$

In the ground ($5s_{1/2}$) electronic level of Rb, $H_m$ yields the Breit-Rabi formula[2] for the energies of the $(m_I,m_J)$ states. Here we are interested instead in the effect of $H_{\mathrm{hfs}}$ in admixing higher electronic levels. In third-order perturbation theory, the shift of interest is

$$E^{(3)}=\sum_{\gamma',\gamma''\neq\gamma}\frac{\langle\gamma|H_{\mathrm{hfs}}|\gamma'\rangle\langle\gamma'|H_B|\gamma''\rangle\langle\gamma''|H_{\mathrm{hfs}}|\gamma\rangle}{(E_\gamma-E_{\gamma'})(E_\gamma-E_{\gamma''})}-\sum_{\gamma'\neq\gamma}\frac{\langle\gamma|H_{\mathrm{hfs}}|\gamma'\rangle\langle\gamma'|H_{\mathrm{hfs}}|\gamma\rangle}{(E_\gamma-E_{\gamma'})^2}\langle\gamma|H_B|\gamma\rangle, \tag{2}$$

where $\gamma$ stands for $(n,l,j,m_J,m_I)$. The main contribution in Eq. (2) comes from $n's$ states coupled in by the contact term in the hfs interaction, although the $n'd$ states also contribute a small effect through the tensor hfs term. Retaining only the dominant $n's$ contribution, factoring out the radial portion, and ignoring the $g_I\mathbf{I}\cdot\mathbf{B}$ term in $H_B$, we obtain

$$E^{(3)}=(\tfrac{8}{3}\pi\mu_B^2 g_I g_J)^2\sum_{n'\neq5}\frac{|\langle5s|\delta(r)/(4\pi r^2)|n's\rangle|^2}{(E_{5s}-E_{n's})^2}$$
$$\times\sum_{m',m''}\mu_B g_J\langle m|\mathbf{I}\cdot\mathbf{J}|m'\rangle[\langle m'|\mathbf{J}\cdot\mathbf{B}|m''\rangle\langle m''|\mathbf{I}\cdot\mathbf{J}|m\rangle-\langle m'|\mathbf{I}\cdot\mathbf{J}|m\rangle\langle m|\mathbf{J}\cdot\mathbf{B}|m\rangle], \tag{3}$$

where $m$ stands for $(m_I,m_J)$. With use of completeness and some operator algebra[3] (with $\mathbf{J}=\boldsymbol{\sigma}/2$), the sum over $m'$ and $m''$ in Eq. (3) becomes

$$\tfrac{1}{4}\mu_B g_J\langle m_I m_J|[(2\mathbf{I}\cdot\mathbf{B})\mathbf{I}\cdot\mathbf{J}-2I^2\mathbf{J}\cdot\mathbf{B}+\mathbf{I}\cdot\mathbf{B}]|m_I m_J\rangle.$$

Taking the quantization axis along $\mathbf{B}$, Eq. (3) may now be written in the form

$$E^{(3)}=\tfrac{1}{2}g_J\mu_B B\sum_{n'\neq5}\frac{a_{5s}a_{n's}}{(\nu_{5s}-\nu_{n's})^2}[m_I^2 m_J-I(I+1)m_J+m_I/2], \tag{4}$$

 

where $\nu_{ns} = E_{ns}/h$ and $a_{ns}$ is the hyperfine interval in state $ns$ given by

$$a_{ns} \equiv \frac{8\pi\mu_B^2 g_I g_J}{3h} |\psi_{ns}(0)|^2. \tag{5}$$

In the experiment of Fletcher, Lipson, and Larson, the terms in Eq. (4) that contain only $m_I$ or $m_J$ would probably be absorbed into the Breit-Rabi formula within uncertainties, while the term in $m_I^2 m_J$ would yield a distinguishable effect just as they observe. Defining $\beta$ as the coefficient of this term,

$$E^{(3)}/h = \beta m_I^2 m_J B/J, \tag{6}$$

we have

$$\beta = \frac{g_J\mu_B}{4h} \sum_{n'\neq 5} \frac{a_{5s}a_{n's}}{(\nu_{5s}-\nu_{n's})^2}. \tag{7}$$

The sum in Eqs. (4) and (7) extends over all discrete and continuum $n's$ states. We evaluate it using the Fermi-Segrè approximation,[4] in which we can write[5]:

$$|\psi_{ns}(0)|^2 = \frac{Z}{\pi(n-\delta_0)^3 r_0^3}, \tag{8}$$

where $Z$ is the nuclear charge, $r_0$ is the Bohr radius, and $\delta_0$ is the quantum defect for $s$ states. Since $E_n = -hcR/(n-\delta_0)^2$, the discrete part of the sum in Eq. (7) for $n' > 5$ becomes

$$\beta[\text{discrete}]_{n'>5} = \frac{g_J\mu_B}{4h}\frac{a_{5s}^2}{(\nu_{5s}-\nu_{6s})^2}\left[\frac{5-\delta_0}{6-\delta_0}\right]^3 \left[1 + \sum_{n'\geq 7} \frac{(n'-\delta_0)(11-2\delta_0)^2}{(6-\delta_0)(n'-5)^2(n'-2\delta_0+5)^2}\right]. \tag{9}$$

Using the measured values $\delta_0 = 3.2$, $a_{5s} = 1.0$ GHz, and $\nu_{6s} - \nu_{5s} = 6.0\times 10^5$ GHz for $^{85}$Rb, the value $2.8\times 10^{10}$ Hz/T for $g_J\mu_B/h$, and summing the series in Eq. (9), we obtain

$$\beta[^{85}\text{Rb discrete}]_{n'\geq 5} = 0.008 \text{ Hz/T}. \tag{10}$$

To this must be added the contribution of the hole states $n' < 5$. For these states the probability density at the origin builds up much less rapidly than the energy (squared) denominator, and the only significant addition to $\beta$ comes from $n' = 4$, which we calculate from published Hartree-Fock values[6] for $E_{4s}$ and $\psi(0)$:

$$\beta[^{85}\text{Rb discrete}]_{n'\leq 4} = 0.002 \text{ Hz/T}. \tag{11}$$

To calculate the contribution of the continuum in Eq. (7), I begin with the energy-normalized density at the origin for $s$-state Coulomb wave functions[7] of energy $E > 0$,

$$|\psi_{Es}^{(c)}(0)|^2 dE = \frac{1}{\pi r_0^2 e^2}\frac{dE}{1-\exp[-2\pi\hbar/r_0(2mE)^{1/2}]}. \tag{12}$$

We renormalize this density at $E = 0$ to agree with the corresponding bound-state expression [using Eq. (8)] as $n \rightarrow \infty$,

$$|\psi_{Es}(0)|^2 dE \underset{E\rightarrow 0}{=} |\psi_{ns}(0)|^2 \frac{dn}{dE} dE = \frac{Z\,dE}{\pi r_0^2 e^2}, \tag{13}$$

which simply requires us to multiply the density in Eq. (12) by a factor of $Z$, just as one would expect with continuum states in the Fermi-Segrè approximation. This approximation should apply in the range of $E$ of interest. The continuum contribution to $\beta$ in Eq. (7) thus becomes, with the aid of Eqs. (5), (8), and $h\nu_{5s} = e^2/2r_0(5-\delta_0)^2$,

$$\beta[\text{continuum}] = \frac{g_J\mu_B h a_{5s}}{4}\frac{8\pi\mu_B^2 g_I g_J}{3h}\int_0^\infty \frac{Z|\psi_{Es}^{(c)}(0)|^2}{(E_{5s}-E)^2} dE$$
$$= \frac{g_J\mu_B a_{5s}^2(5-\delta_0)}{8h\nu_{5s}}\int_0^\infty d\nu \frac{1}{(\nu_{5s}-\nu)^2(1-\exp\{[h/(2mr_0^2\nu)]^{1/2}\})}, \tag{14}$$

which yields

$$\beta[^{85}\text{Rb continuum}] = 0.006 \text{ Hz/T}. \tag{15}$$

Combining the various contributions to $\beta$ from Eqs. (10), (11), and (15), we obtain our theoretical value for $\beta$ in $^{85}$Rb:

$$\beta(^{85}\text{Rb})_{\text{theory}} = 0.016 \text{ Hz/T}. \tag{16}$$

The value for $^{87}$Rb scales up exactly as $g_I^2$:

$$\beta(^{87}\text{Rb})_{\text{theory}} = 0.18 \text{ Hz/T}. \tag{17}$$

These values are to be compared with the experimental ones quoted above in the first paragraph.

In conclusion, I have shown that the hyperfine interaction, by mixing excited states of opposite spin direction into the ground state, accounts very well for the Zeeman shift in Rb discovered by Fletcher, Lipson, and Larson. The uncertainty in this calculation should be less than 15%, judging by success of the Fermi-Segrè treatment of alkali-metal-atom hyperfine structure. It should be noted also that some of the inaccuracies in the Fermi-Segrè approximation cancel in the ratios used here [e.g., in Eqs. (9) and (14)] to find the answer in terms of measured quantities. A more rigorous approach is under consideration using Hartree-Fock wave functions.

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[2]N. F. Ramsey, *Molecular Beams* (Oxford Univ. Press, London, 1956).

[3]The relation $(\boldsymbol{\sigma}\cdot\mathbf{a})(\boldsymbol{\sigma}\cdot\mathbf{b})=\mathbf{a}\cdot\mathbf{b}+i\boldsymbol{\sigma}\cdot\mathbf{a}\times\mathbf{b}$ is applied repeatedly, together with $\mathbf{I}\times\mathbf{I}=i\mathbf{I}$.

[4]E. Fermi and E. Segrè, Z. Phys. **82**, 729 (1933); see also, M. Mizushima, *Quantum Mechanics of Atomic Spectra and Atomic Structure* (Benjamin, New York, 1970).

[5]We omit from the right side of Eq. (8) the factor $(1-d\delta_0/dn)$ and a relativistic correction. Both of these contributions are small, and should vary so slowly with $n$ as to make a negligible change in the ratios used to obtain numerical answers.

[6]C. Froese Fischer, *The Hartree-Fock Method for Atoms: A Numerical Approach* (Wiley, New York, 1977).

[7]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1965).