Equation (B.22) in (B.8) yields the desired matrix element for $k_1=k_2=k$. Note that by (B.17) and the definitions after (B.5) the dimensional radial integral in (B.8) is given in terms of the nondimensional integral (B.22) by

$$\frac{eH}{2}\int_0^\infty (f_1g_2+f_2g_1)r^3dr=\mu_0H\frac{1}{\gamma}\int_0^\infty (F_1G_2+F_2G_1)\rho^3d\rho. \qquad \text{(B.23)}$$

For $k_1\neq k_2$, as in (B.9), the more complicated (B.15) appears to be necessary. The Breit-Margenau result (70) for a Coulomb field is obtained by setting $n_1=n_2$ and

$$\int_0^\infty G_1{}^{(0)2}\rho d\rho=(1/\rho)_{nn}=1/n^2 \qquad \text{(B.24)}$$

in (B.22). The matrix element $(1/\rho)_{n_1n_2}$ on the right hand side in (B.22) is given by Eqs. (A.4, 7) in Appendix A.

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Relativistic Contributions to the Magnetic Moment of n-Electron Atoms

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A Schrödinger-Pauli approximation wave equation for an n-electron atom in an external magnetic field H is derived from a Dirac equation by straightforward extension of the procedure for $n=2$. The order α^2 terms in the resulting Hamiltonian contain corresponding $\alpha^2\mu_0H$ and α^2Ry (fine structure) parts. The $\alpha^2\mu_0H$ terms can be arranged as a sum of the existing relativistic bound state contributions due to Breit, Margenau, and Lamb, and an additional contribution. The additional contribution is analogous to the spin-orbit contribution to fine structure. In the $^2S_{\frac{1}{2}}$ ground state of the heavier alkalies it is estimated to yield a positive contribution to the atomic g value of the order of ten times the aforementioned (negative) contributions, which may help to account for some experimental results.

INTRODUCTION

PRECISION measurements of the Zeeman effect by atomic beam spectroscopy[1] have yielded deviations from unity of the g_J values of the heavier alkali atoms in their ground state, $^2S_{\frac{1}{2}}$. The relevant experimental results are:

rubidium relative to sodium,

$$(g_J)_{\mathrm{Rb}}/(g_J)_{\mathrm{Na}}=1+5\times10^{-5}; \qquad \text{(1a)}$$

cesium relative to sodium,

$$(g_J)_{\mathrm{Cs}}/(g_J)_{\mathrm{Na}}=1+13.4\times10^{-5}, \qquad \text{(1b)}$$

with a statistical probable error of approximately $\pm1\times10^{-5}$. The g_J of lithium, sodium, and potassium were found to be identical to within $\pm2.5\times10^{-5}$. An additional measurement is reported by Franken and Koenig:[2]

potassium relative to hydrogen,

$$(g_J)_{\mathrm{K}}/(g_J)_{\mathrm{H}}=1+(1.6\pm0.4)\times10^{-5}. \qquad \text{(2)}$$

The results (1) and (2) have so far not been quantitatively explained (i.e., to the experimental accuracy), nor will they be in this paper. A qualitative interpretation of at least part of the effects involved will however be added to the existing one.[3]

The deviations from unity in (1) and (2) should be attributable to relativistic effects inasmuch as nonrelativistic theory predicts $g_J=1$ in a $^2S_{\frac{1}{2}}$ state. Quantum-electrodynamic self-radiative effects on a single free electron, producing an altered "intrinsic" magnetic moment of the electron,[4] would be expected to affect similar Zeeman levels of one-electron spectra similarly and hence to yield no deviations from unity in the ratios (1) and (2). Of the various bound-state relativistic effects, i.e., effects arising from the atom obeying a relativistic rather than a nonrelativistic wave equation, those due to Breit and Margenau[5] and to Lamb[6] appear too small by a factor of the order of ten.[7] However effects of breakdown of Russell-Saunders coupling by a combination of electrostatic interaction and spin-orbit coupling mixing states of higher configurations into the ground state have been estimated by Phillips[3] to yield differing amounts to the magnetic moments of the alkalis of the right order of magnitude to account for at least part of (1) and (2).

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[1] P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

[2] P. Franken and S. Koenig, Phys. Rev. **88**, 199 (1952).

[3] M. Phillips, Phys. Rev. **88**, 202 (1952).

[4] J. Schwinger, Phys. Rev. **82**, 664 (1951); R. Karplus and N. M. Kroll, Phys. Rev. **77**, 536 (1950).

[5] G. Breit, Nature **122**, 649 (1928); H. Margenau, Phys. Rev. **57**, 383 (1940); N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 72.

[6] W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).

[7] See W. Perl and V. Hughes (preceding paper) [Phys. Rev. **91**, 842 (1953)] for an evaluation of these effects in $^3S_1$ helium.

In this paper another possible source of at least part of (1) and (2) will be indicated by an examination of the $\alpha^2\mu_0 H$ terms in an n-electron Schrödinger-Pauli approximation wave equation derived from an n-electron Dirac-type wave equation (α= fine structure constant, μ_0= Bohr magneton, H= external magnetic field strength). These terms arise analogously to the usual α^2Ry, or fine structure, terms (Ry = Rydberg energy), and like the latter can be grouped into a "relativistic increase of mass" term (R), a "spin-orbit" term (S) and a "Breit interaction" term (B). Term (B) contains the diamagnetic contribution of Lamb. In application to alkali ground states, (R)+(S) can be rearranged to give the Breit-Margenau contribution for the valence electron in an effective central field together with a residual term (+), which is the indicated source in question. (+) is analogous to the spin-orbit fine structure term for one-electron spectra. It yields positive increments to atomic g values, in distinction to the negative increments given by the Breit-Margenau and Lamb contributions. A rough estimate of the magnitude of term (+) for the heavier alkalis yields the order of magnitude in (1). Some data for ^2P states will also be discussed.

THE WAVE EQUATION

The relativistic Hamiltonian for the stationary states of an n-electron atom is taken as a sum of n one-electron Dirac Hamiltonians and $n(n-1)/2$ interelectronic Coulomb plus Breit interactions. Thus

$$\{E-V+\sum_{k=1}^{n}[\beta_k+\boldsymbol{\alpha}_k\cdot(\mathbf{p}_k+e\mathbf{A}_k)]+\sum_{l>k=1}^{n}B_{kl}\}U=0, \quad (3)$$

in which E is the stationary state energy including the rest energy of the n electrons, V is the sum of the electrostatic interactions,

$$V=\sum_{k=1}^{n}V_k(r_k)+\sum_{l>k=1}^{n}V_{kl}(r_{kl}) \quad (4)$$

$$=-\sum_{k=1}^{n}\frac{Ze^2}{r_k}+\sum_{l>k=1}^{n}\frac{e^2}{r_{kl}}, \quad (5)$$

$\mathbf{p}_k$ is the momentum of the kth electron, $\mathbf{A}_k$ is the given vector potential field at the kth electron, $\boldsymbol{\alpha}_k$, β_k are the usual Dirac variables, and B_{kl} is the Breit interaction[8] between kth and lth electrons,

$$B_{kl}=\frac{e^2}{2r_{kl}}\left(\boldsymbol{\alpha}_k\cdot\boldsymbol{\alpha}_l+\frac{\boldsymbol{\alpha}_k\cdot\mathbf{r}_{kl}\boldsymbol{\alpha}_l\cdot\mathbf{r}_{kl}}{r_{kl}^2}\right), \quad (6)$$

with $\mathbf{r}_{kl}=\mathbf{r}_k-\mathbf{r}_l$, the vector distance between kth and lth electrons. In (3), E, V, $e\mathbf{A}_k$ and B_{kl} are expressed in units mc^2 and $\mathbf{p}_k$ in units mc. The stationary state wave function U depends on n space coordinates $\mathbf{r}_k$ and n spinor variables. Each spinor variable takes on four values, 1, 1′, 2, 2′, say. Apart from non-Coulombic nuclear effects, which will be neglected, and electron self-radiative effects, which can be included separately if desired,[7] and subject to Breit's prescription for the use of B_{kl}, discussed later, Eq. (3) will be considered correct to order α^2.

The reduction of (3) to Schrödinger-Pauli form to order α^2 can be accomplished by straightforward extension of the procedure[7,8] for $n=2$. First, U is represented by a "column matrix." Each position in the column matrix corresponds to a component of U characterized as follows: U_0 is the component of U corresponding to the value of either 2 or 2′ for all n Dirac spinor variables; U_k is the component of U corresponding to value 1 or 1′ of the kth spinor variable, the remaining $n-1$ spinor variables having values 2 or 2′; U_{kl} is the component of U corresponding to values 1 or 1′ of the kth and lth spinor variables, the remaining $n-2$ having values 2 or 2′; etc. By operating on the column matrix for U with the Dirac matrices

$$\beta_k=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}_k,\quad \boldsymbol{\alpha}_k=\boldsymbol{\sigma}_k\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}_k,\quad k=1,\cdots n, \quad (7)$$

where $\boldsymbol{\sigma}_k$ is the usual Pauli spin variable, a series of equations relating various components of U is obtained, one equation for each position in the column matrix. From this series of equations it is seen that for a positive energy state the 1,1′ components of U for any spinor variable are small, relative to the 2,2′ components by the order of magnitude $R=p+eA\sim\alpha(1+\mu_0H/\text{Ry})$. Thus, relative to the largest component of U, namely U_0, we have $U_k\sim RU_0$, $U_{kl}\sim R^2U_0$ (plus terms in M_{kl}, see below), etc. To obtain a Schrödinger-Pauli equation for U_0 with a Hamiltonian correct to the independent orders of magnitude α^2Ry and $\alpha^2\mu_0H$, only expressions for U_k to order R^3U_0 and for U_{kl} to order R^2U_0 are needed, and to obtain these, only U components with up to three subscripts U_{klm} need be considered. From all but one of the resulting equations for U_0, U_k, U_{kl}, we obtain the desired expression of small U components in terms of the largest:

$$U_k=[-(2+W-V)^{-1}R_k-\tfrac{1}{8}R_k\sum_{l=1}^{n}{}'R_l^2$$
$$+\tfrac{1}{8}\sum_{l=1}^{n}{}'(R_lM_{kl}+2M_{kl}R_l)]U_0, \quad (8)$$

$$U_{kl}=\tfrac{1}{4}(R_kR_l-M_{kl})U_0, \quad (9)$$

in which $\sum'_l$ denotes a summation over l omitting $l=k$, $W=E-n$ is the state energy minus the rest energy of the n electrons,

$$R_k=\boldsymbol{\sigma}_k\cdot(\mathbf{p}_k+e\mathbf{A}_k), \quad (10)$$

and

$$M_{kl}=\frac{e^2}{2r_{kl}}\left(\boldsymbol{\sigma}_k\cdot\boldsymbol{\sigma}_l+\frac{\boldsymbol{\sigma}_k\cdot\mathbf{r}_{kl}\boldsymbol{\sigma}_l\cdot\mathbf{r}_{kl}}{r_{kl}^2}\right). \quad (11)$$

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[8] G. Breit, Phys. Rev. **34**, 553 (1929); **39**, 616 (1932).

Substituting (8) and (9) into the remaining equation mentioned above yields, for the largest component, U_0:

$$\Big[-W+V+\sum_{k=1}^{n} R_k(2+W-V)^{-1}R_k+\tfrac{1}{4}\sum_{l>k=1}^{n} R_k^2R_l^2 -\tfrac{1}{4}\sum_{l>k=1}^{n}(R_kR_lM_{kl}+M_{kl}R_kR_l+R_kM_{kl}R_l+R_lM_{kl}R_k) +\tfrac{1}{4}\sum_{l>k=1}^{n} M_{kl}M_{kl}\Big]U_0=0. \quad (12)$$

Equation (12) is the same result as for two electrons[8] except summed over all electrons or pairs of electrons. The terms in (12) involving M_{kl} arise from the Breit interaction (6). Of these, the last one is quadratic in M_{kl} (although of order α^2Ry with $r_{kl}\sim$Bohr radius) and must be dropped, as being in conflict with experiment and with more complete theory taking account of higher order electron interactions.[8,9] [This term does not appear if the M_{kl} dependent terms in (12) are calculated in accordance with Breit's prescription as an expectation value of (6) in the state U and using (8) and (9). In any event this term does not contain the external field and hence would not contribute to the external magnetic interaction energy to order $\alpha^2\mu_0H$.] Equation (12) without the last term is still not a Schrödinger eigenvalue equation as it contains the eigenvalue W in two places. W is therefore eliminated in the second term, using the lowest-order, nonrelativistic, part of (12). Thus, to order α^2,

$$(2+W-V)^{-1}=\tfrac{1}{2}+\tfrac{1}{4}(V-W), \quad (13)$$

and, upon assuming a Schrödinger representation,

$$R_k(2+W-V)^{-1}R_k=\tfrac{1}{2}R_k^2+\tfrac{1}{4}R_k(V-W)R_k, \quad (14)$$

$$=\tfrac{1}{2}R_k^2+\tfrac{1}{4}[(V-W)R_k-i\hbar\boldsymbol{\sigma}_k\cdot\boldsymbol{\nabla}_kV]R_k, \quad (15)$$

in which $-i\hbar\boldsymbol{\nabla}$ is expressed in units of mc. The lowest-order part of (12), i.e., the nonrelativistic Schrödinger equation,

$$\Big(-W+V+\tfrac{1}{2}\sum_{l=1}^{n} R_l^2\Big)U^0=0, \quad (16)$$

may now be substituted into (15), [the $O(\alpha^2)$ difference between U_0 and U^0 is immaterial for this purpose; also, the term produced by this substitution can only be used as a matrix element], to give in place of (12), the desired Schrödinger-Pauli-approximation equation,

$$\Big[-W+V+\tfrac{1}{2}\sum_{k=1}^{n} R_k^2-\tfrac{1}{8}\sum_{k=1}^{n} R_k^4-\frac{i\hbar}{4}\sum_{k=1}^{n}\boldsymbol{\sigma}_k\cdot(\boldsymbol{\nabla}_kV)R_k -\tfrac{1}{4}\sum_{l>k=1}^{n}(R_kR_lM_{kl}+M_{kl}R_kR_l +R_kM_{kl}R_l+R_lM_{kl}R_k)\Big]U_0=0. \quad (17)$$

The first three terms in (17) constitute the usual nonrelativistic Schrödinger Hamiltonian, for, omitting summation signs for brevity,

$$R_k^2=\boldsymbol{\sigma}_k\cdot(\mathbf{p}_k+e\mathbf{A}_k)\boldsymbol{\sigma}_k\cdot(\mathbf{p}_k+e\mathbf{A}_k) \quad (18)$$

$$=p_k^2+e\mathbf{A}_k\cdot\mathbf{p}_k+e\hbar\boldsymbol{\sigma}_k\cdot\mathbf{H}_k+e^2A_k^2, \quad (19)$$

and

$$\tfrac{1}{2}R_k^2=p_k^2/2m+\mu_0(\mathbf{L}_k+\boldsymbol{\sigma}_k)\cdot\mathbf{H}+A_k^2e^2/2mc^2. \quad (20)$$

Equation (19) corresponds to an arbitrary external vector potential $\mathbf{A}_k$, and (20) to a constant uniform external magnetic field. Equation (20) has been made dimensional by dividing p by mc, eA by mc^2 and multiplying through by mc^2. The fourth term in (17) is the "relativistic increase of mass" (R) term. It becomes, upon squaring (19) and retaining only terms linear in the constant uniform magnetic field H, (right-hand side dimensional)

$$(R)=-\tfrac{1}{8}R_k^4 =-(p_k^4/8m^3c^2)-(\mu_0/2m^2c^2)(\mathbf{L}_k+\boldsymbol{\sigma}_k)\cdot\mathbf{H}p_k^2. \quad (21)$$

The fifth term in (17), the "spin-orbit" (S) term, becomes (right-hand side dimensional),

$$(S)=-\tfrac{1}{4}i\hbar\boldsymbol{\sigma}_k\cdot(\boldsymbol{\nabla}_kV)R_k =(\hbar/4m^2c^2)(-i\boldsymbol{\nabla}_kV\cdot\mathbf{p}_k+\boldsymbol{\sigma}_k\cdot\boldsymbol{\nabla}_kV\times\mathbf{p}_k +\boldsymbol{\sigma}_k\cdot\boldsymbol{\nabla}_kV\times\mathbf{A}_ke/c), \quad (22)$$

in which the term $-ie\hbar\boldsymbol{\nabla}_kV\cdot\mathbf{A}_k/c$ has been omitted as vanishing when summed over k in a constant uniform magnetic field. The last set of summed terms (B) in (17), arising from the Breit interaction, can be written, with

$$R_k=P_k+A_k, \quad P_k=\boldsymbol{\sigma}_k\cdot\mathbf{p}_k, \quad A_k=\boldsymbol{\sigma}_k\cdot\mathbf{A}_k, \quad (23)$$

and omitting terms quadratic in A_k, A_l, as

$$(B)=-\tfrac{1}{4}[P_kP_lM_{kl}+M_{kl}P_kP_l+P_kM_{kl}P_l+P_lM_{kl}P_k] -\tfrac{1}{4}e[(A_kP_l+A_lP_k)M_{kl}+M_{kl}(A_kP_l+A_lP_k) +(A_kM_{kl}P_l+P_kM_{kl}A_l) +(A_lM_{kl}P_k+P_lM_{kl}A_k)]. \quad (24)$$

The first bracketed term in (24), an α^2Ry or fine structure contribution, is reduced explicitly by Breit.[8,10] The second bracketed term in (24), the Breit interaction contribution to $\alpha^2\mu_0H$, is reduced explicitly in the preceding paper.[7]

The three terms (21), (22), and (24) are seen to contain corresponding α^2Ry and $\alpha^2\mu_0H$ contributions. This correspondence is not surprising, in view of the occurrence of $\mathbf{A}_k$ in the Dirac Hamiltonian (3) only in the combination $\mathbf{p}_k+e\mathbf{A}_k$. Inasmuch as this combination occurs also in the classical Hamiltonian and equations of motion for electrons, the effect of a given external vector potential may be regarded classically as inducing the diamagnetic momentum $e\mathbf{A}_k$ in electron k to give

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[9] G. E. Brown and D. G. Ravenhall, Proc. Roy. Soc. (London) **A208**, 552 (1951); E. E. Salpeter, Phys. Rev. **87**, 328 (1952).

[10] H. Bethe, *Handbuch der Physik* (Verlag. Julius Springer, Berlin, Germany, 1933), Vol. 24/1, second edition, 377.

it the total momentum $\mathbf{p}_k+e\mathbf{A}_k$. A general diamagnetic classical interpretation for magnetic interaction energies is thus possible. For example, the usual nonrelativistic contribution of order μ_0H has the well-known classical interpretation of diagmagnetically induced kinetic energy due to the product of mechanical momentum $\mathbf{p}$ and the diamagnetically induced momentum $e\mathbf{A}$ ($\mathbf{p}$ may be taken as the original momentum for $\mathbf{A}=0$ if $e\mathbf{A}/c\ll\mathbf{p}$); the ($R$) contribution (21) to $\alpha^2\mu_0H$ is due to "relativistic increase of mass" in which one factor of the fourth power momentum term is diamagnetically induced momentum; the (S) contribution (22) to $\alpha^2\mu_0H$ has the classical spin-orbit energy explanation with $e\mathbf{A}$ replacing $\mathbf{p}$; Lamb's diamagnetic contribution is shown later to be the "spin k-orbit l" part of the (B) term (24) with $e\mathbf{A}$ replacing $\mathbf{p}$; etc. Likewise one sees from this point of view that spin-spin contributions to fine structure have no analogous $\alpha^2\mu_0H$ contributions.

Equations (20), (21), (22), and (24) yield by first order perturbation theory the linear-in-H contribution ΔE_H to the energy eigenvalue of an n-electron atom governed by (17) as

$$\Delta E_H=\Delta E_N+\Delta E_R+\Delta E_S+\Delta E_B, \tag{25}$$

where, for a constant uniform magnetic field $\mathbf{H}$ the nonrelativistic contribution is

$$\Delta E_N=\mu_0\langle\Psi|\mathbf{H}\cdot\sum_{k=1}^{n}(\mathbf{L}_k+\boldsymbol{\sigma}_k)|\Psi\rangle; \tag{26}$$

the "relativistic increase of mass" contribution is

$$\Delta E_R=-\frac{\mu_0}{2}\langle\Psi|\mathbf{H}\cdot\sum_{k=1}^{n}(\mathbf{L}_k+\boldsymbol{\sigma}_k)p_k^2|\Psi\rangle; \tag{27}$$

the "spin" contribution is

$$\Delta E_S=\frac{\mu_0}{2}\langle\Psi|\sum_{k=1}^{n}\boldsymbol{\sigma}_k\cdot\boldsymbol{\nabla}_kV\times\mathbf{A}_k|\Psi\rangle; \tag{28}$$

the Breit interaction contribution is given by Eq. (60) of reference 7,

$$\begin{aligned}\Delta E_B=\Big\langle\Psi\Big|\sum_{l>k=1}^{n}\Big\{-\frac{e}{2}\frac{e^2}{r_{kl}}\Big[\mathbf{A}_k\cdot\Big(1+\frac{\mathbf{r}_{kl}\mathbf{r}_{kl}}{r_{kl}^2}\Big)\cdot\mathbf{p}_l\\ +\mathbf{A}_l\cdot\Big(1+\frac{\mathbf{r}_{kl}\mathbf{r}_{kl}}{r_{kl}^2}\Big)\cdot\mathbf{p}_k\Big]\\ +\mu_0\frac{e^2}{r_{kl}^3}(\boldsymbol{\sigma}_k\cdot\mathbf{r}_{kl}\times\mathbf{A}_l+\boldsymbol{\sigma}_l\cdot\mathbf{r}_{lk}\times\mathbf{A}_k)\Big\}\Big|\Psi\Big\rangle,\end{aligned} \tag{29}$$

and Ψ satisfies (17). In (28) V is given by (4) and later specialized to (5). The unit for p_k is mc and for V and e^2/r_{kl} is mc^2.

The expectation value ΔE_H, Eqs. (25) to (29), results also from a reduction to Schrödinger-Pauli form of

$$-e\langle U|\sum_{k=1}^{n}\boldsymbol{\alpha}_k\cdot\mathbf{A}_k|U\rangle, \tag{30}$$

in which U satisfies the Dirac equation (3) without $\mathbf{A}_k$. This procedure, followed in reference 7 for $n=2$, requires an $O(\alpha^2)$ normalization correction for Ψ, necessitated by the normalization assumption $\langle U|U\rangle=1$ in (30). The derivation of the eigenvalue equation (17), which is presumably correct to the orders α^2Ry, $\alpha^2\mu_0H$, did not however require a normalization assumption. Since also an eigenvalue is independent of the normalization of its eigenfunction, ΔE_H as obtained from (17) to order $\alpha^2\mu_0H$, being the contribution to the eigenvalue of (17) to this order, should be and is independent of the normalization of Ψ. It would thus appear that the use by Lamb[11] of normalization in this connection is an error which, however, leads to the right answer because of his compensating error of using, in effect, p^2 instead of R^2 in (16) to yield (17).

For one bound electron, ΔE_R, in Eq. (21), combines with ΔE_S, in Eq. (22), to give the Breit-Margenau result,[5] as noted by Lamb,[11] just as the corresponding fine structure contributions combine to give the Sommerfeld-Dirac fine structure formula. This correspondence extends also to relative sign of the contributions. Thus, for hydrogenic S states, contribution (R) to fine structure is negative, contribution (S) is positive,[12] the ratio being $[(S)/-(R)]_{fs}=n/(2n-\frac{3}{4})$ or $\frac{4}{5}$ for $n=1$ to $\frac{1}{2}$ for $n=\infty$ in state ${}^2S_{\frac{1}{2}}$. Similarly,[7] contribution (R) to $\alpha^2\mu_0H$ is negative, contribution (S) is positive, the ratio being $[(S)/-(R)]_H=\frac{1}{3}$ in state ${}^2S_{\frac{1}{2}}$ independently of principal quantum number.

In evaluating (26) to (29), the state Ψ should be, by first order perturbation theory, an eigenstate of (17) without the vector potential $\mathbf{A}_k$ terms. Hence, Ψ can be expressed in the Russell-Saunders scheme as

$$\Psi=\Psi_0+\alpha^2\textstyle\sum_m c_m\Psi_m, \tag{31}$$

where the Ψ_m and Ψ_0 are Russell-Saunders eigenfunctions of (16) without the vector potential terms,

$$(-W_m+V+\tfrac{1}{2}\sum_{k=1}^{n}p_k^2)\Psi_m=0, \tag{32}$$

and the order α^2 arises from the α^2Ry terms in (17). By the same argument as in the two-electron case[7] the Ψ_m contribute only in order $\alpha^4\mu_0H$ in (26) to (29) and so the $\alpha^2\mu_0H$ contributions are given by (27) to (29) with Ψ replaced by Ψ_0. One cannot however conclude that the $\alpha^4\mu_0H$ contributions are negligible relative to the $\alpha^2\mu_0H$ contributions. This is true only if c_m in (31) does not change the order of magnitude by being $\gg1$.

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[11] W. E. Lamb, Jr., Phys. Rev. **85**, 259 (1952).

[12] See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 120 and following.

In light atoms, as in the two-electron case,[7] $c_m \lesssim 1$. However c_m increases rapidly with atomic number and for the heavier alkalis Phillips[3] has estimated the $\alpha^4 c_m^2 \mu_0 H$ contributions arising from the diagonal product terms of (26) using (31) as being of the same order as $\alpha^2\mu_0 H$. Hence, for the heavier alkalis $\alpha^2 c_m^2 \sim 1$ or $c_m \sim 1/\alpha$. The diagonal product terms in (27) to (29) for $\Psi=\Psi_0$ will be considered in the next section. Lastly, the cross-product terms in (27) to (29) of type $\langle\Psi_0|\alpha^2\mu_0 H|\alpha^2 c_m \Psi_m\rangle$ are of order $\alpha^4 c_m \mu_0 H$ and hence of order $\alpha^3\mu_0 H$ using Phillips' result. It may be concluded that the first neglected order for the heavier alkalis (aside from self-radiative effects) is $\alpha^3\mu_0 H$ (in contrast to $\alpha^4\mu_0 H$ for light atoms), which is negligible in the present problem.

APPLICATION TO ALKALI GROUND STATES

Consider the sum of the $\alpha^2\mu_0 H$ contributions (27) to (29) for the Z-electron configuration of one valence electron outside closed shells. In (29) and that part of (28) involving pairs of electrons, neglect the exchange contributions due to the antisymmetry of Ψ. Then the summations in (27) and (28) reduce to one term, that for the valence electron, denoted by subscript 1, and the summation in (29) reduces to one over those electron pairs of which the valence electron is a member. Thus the $\alpha^2\mu_0 H$ contributions for a one-valence-electron configuration become approximately

$$\begin{aligned}\Delta E_{RSB} &= \Delta E_R + \Delta E_S + \Delta E_B \\ &= \mu_0 \Big\langle \Psi_0 \Big| -\tfrac{1}{2}\mathbf{H}\cdot(\mathbf{L}_1+\boldsymbol{\sigma}_1)p_1^2 + \tfrac{1}{2}\boldsymbol{\sigma}_1\cdot\nabla_1 V\times\mathbf{A}_1 \\ &\quad + \sum_{i=2}^{Z}\Big[\frac{e^2}{r_{1i}^3}\boldsymbol{\sigma}_1\cdot\mathbf{r}_{1i}\times\mathbf{A}_i \\ &\qquad -\frac{e^2}{\hbar r_{1i}}\mathbf{A}_i\cdot\Big(1+\frac{\mathbf{r}_{1i}\mathbf{r}_{1i}}{r_{1i}^2}\Big)\cdot\mathbf{p}_1\Big]\Big|\Psi_0\Big\rangle, \end{aligned} \tag{33}$$

where Ψ_0 is the relevant Russell-Saunders eigenfunction of (32). The second term ΔE_S in (33) is rearranged as follows: by (4),

$$\nabla_1 V = \nabla_1 V_1 + \sum_{i=2}^{Z} \nabla_1 V_{1i} = \frac{1}{r_1}\frac{\partial V_1}{\partial r_1}\mathbf{r}_1 + \sum_{i=2}^{Z}\frac{1}{r_{1i}}\frac{\partial V_{1i}}{\partial r_{1i}}\mathbf{r}_{1i}. \tag{34}$$

Write

$$V_1(r_1) = V_c(r_1) + [V_1(r_1) - V_c(r_1)], \tag{35}$$

where $V_c(r_1)$ is to represent an effective central field acting on the valence electron 1. Also write

$$\mathbf{A}_1 = (\mathbf{A}_1 - \mathbf{A}_i) + \mathbf{A}_i = \tfrac{1}{2}(\mathbf{H}\times\mathbf{r}_{1i} - \mathbf{H}\times\mathbf{r}_1). \tag{36}$$

Then (33) becomes

$$\begin{aligned}\Delta E_{RSB} &= \mu_0\Big\langle \Psi_0\Big| \tfrac{1}{2}[-\mathbf{H}\cdot(\mathbf{L}+\boldsymbol{\sigma})p^2 + \boldsymbol{\sigma}\cdot\nabla V_c\times\mathbf{A}]_1 \\ &\quad + \tfrac{1}{2}[\boldsymbol{\sigma}_1\cdot\nabla_1(V_1-V_c)\times\mathbf{A}_1 + \sum_{i=2}^{Z}\boldsymbol{\sigma}_1\cdot\nabla_1 V_{1i}\times(\mathbf{A}_1-\mathbf{A}_i)] \\ &\quad + \sum_{i=2}^{Z}\Big[\frac{e^2}{2r_{1i}^3}\boldsymbol{\sigma}_1\cdot\mathbf{r}_{1i}\times\mathbf{A}_i \\ &\qquad -\frac{e^2}{\hbar r_{1i}}\mathbf{A}_i\cdot\Big(1+\frac{\mathbf{r}_{1i}\mathbf{r}_{1i}}{r_{1i}^2}\Big)\cdot\mathbf{p}_1\Big]\Big|\Psi_0\Big\rangle. \end{aligned} \tag{37}$$

If $V_c(r_1)$ is taken as a central field potential that gives the correct value of $\langle p_1^2\rangle$, then the first bracket expression in (37) represents the Margenau contribution ΔE_M to $\alpha^2\mu_0 H$ as usually applied.[2] In the last bracket expression in (37), the $\mathbf{p}$ term vanishes for the $\Psi_0={}^2S_{\frac{1}{2}}$ ground state. The first term is just one-half Lamb's diamagnetic contribution,[6] i.e., the spin dependent part of the Breit interaction contribution in (33) is Lamb's contribution ΔE_L, which is halved by use of (36) and (5) in the spin contribution ΔE_S of (33). The second bracket expression in (37), ΔE_+, will next be estimated roughly for the $\Psi_0={}^2S_{\frac{1}{2}}$ ground state. Coulomb potentials (5) are assumed and for the central field potential

$$V_c(r_1) \sim -Z_c e^2/r_1. \tag{38}$$

Then with $\mathbf{H}=(0,0,H)$ and

$$\langle\sigma_{1x}\rangle = \langle\sigma_{1y}\rangle = 0, \quad \langle\sigma_{1z}\rangle = 1, \tag{39}$$

the expression in question gives a $g/2$ value increment of

$$\begin{aligned}(\Delta g/2)_+ = \frac{\Delta E_+}{\mu_0 H} = \frac{1}{4}\Big\langle \frac{(Z-Z_c)e^2}{r_1}\Big(1-\frac{z_1^2}{r_1^2}\Big) \\ -\sum_{i=2}^{Z}\frac{e^2}{r_{1i}}\Big(1-\frac{z_{1i}^2}{r_{1i}^2}\Big)\Big\rangle, \end{aligned} \tag{40}$$

where $z_{1i}=z_1-z_i$ and $\rangle$ represents $|{}^2S_{\frac{1}{2}}\rangle$. Because of the spherical symmetry in the ${}^2S_{\frac{1}{2}}$ state,

$$\langle z_1^2/r_1^3\rangle = \langle\cos^2\theta_1/r_1\rangle = \tfrac{1}{3}\langle 1/r_1\rangle. \tag{41}$$

$\langle z_{1i}^2/r_{1i}^3\rangle$ is estimated by considering the classical geometry of a point electron at $\mathbf{r}_1$ outside spherical shells of radius r_i containing the core electrons uniformly distributed. Taking the polar axis along $\mathbf{r}_1$ and averaging uniformly with respect to all directions of $\mathbf{r}_i$ gives

$$\begin{aligned}\Big\langle\frac{z_{1i}^2}{r_{1i}^3}\Big\rangle &= \Big\langle \int_0^\pi (r_{1i})^{-1}\cos^2\theta_{1i}\sin\theta_i d\theta_i \Big/ \int_0^\pi \sin\theta_i d\theta_i\Big\rangle \\ &= \Big\langle\frac{1}{r_1}\Big(1-\frac{2}{3}\frac{r_i^2}{r_1^2}\Big)\Big\rangle. \end{aligned} \tag{42}$$

Using hydrogenic values to estimate $\langle r_i^2\rangle$ relative to

TABLE I. Estimate of $\alpha^2\mu_0H$ energy contributions in $^2S_{\frac{1}{2}}$ alkali ground states.

Elem.	Z	n	n^*	C	$(\Delta g/2)_+$[a]	$(\Delta g/2)_M$	$\frac{1}{2}(\Delta g/2)_L$	$(\Delta g/2)$[b]	$(\Delta g/2)-(\Delta g/2)_{\mathrm{Na}}$
H	1	1	1	...	0	−1.78	0	−1.78	−4.5
Li	3	2	1.6	0.07	0.8	−0.9	−0.1	−0.2	−2.9
Na	11	3	1.63	0.13	3.9	−1.1	−0.1	2.7	0
K	19	4	1.78	0.15	6.0	−1.0	−0.1	4.9	2.2
Rb	37	5	1.83	0.14	11.8	−1.0	−0.1	10.7	8.0
Cs	55	6	1.9	0.14	16.5	−0.9	−0.1	15.5	12.8

[a] All $(\Delta g/2)$ entries in table are $\times 10^{-5}$.
[b] $(\Delta g/2)=\Delta E_{RSB}/\mu_0H$, Eqs. (37) and (53).

$\langle r_1^2\rangle$, yields

$$\sum_{i=2}^{Z}\frac{r_i^2}{r_1^2}=\sum_{i=2}^{Z}\frac{n_i^2[5n_i^2+1-3l_i(l_i+1)]}{n_1^2[5n_1^2+1]}=(Z-1)C, \qquad (43)$$

where n_i, l_i are, respectively, the hydrogenic principal and azimuthal quantum numbers of a core electron and n_1 is the hydrogenic principal quantum number of the valence electron. The values of C yielded by (43) for the alkali elements are given in Table I. Substituting (41) to (43) in (40) and taking $Z_c=1$ in line with the approximations in (42), (43), (this also normalizes $(\Delta g/2)_+$ to zero for hydrogen), gives

$$(\Delta g/2)_+=\tfrac{1}{6}(Z-1)(1-C)\langle e^2/r_1\rangle \qquad (44)$$

$$=\tfrac{1}{6}(Z-1)(1-C)\langle T-W\rangle, \qquad (45)$$

in which $-\langle e^2/r_1\rangle$ is regarded in this approximation as the potential energy of the valence electron in an equivalent central field with $\langle T\rangle$ and W the corresponding kinetic and total energy respectively, in units mc^2. The Margenau[5] and Lamb[6] contributions to $\alpha^2\mu_0H$ in the same central field are

$$(\Delta g/2)_M=-\tfrac{2}{3}\langle T\rangle, \qquad (46)$$

$$(\Delta g/2)_L=-\tfrac{1}{3}\langle T+W\rangle. \qquad (47)$$

Finally, using Lamb's[6] approximate expression for $\langle T\rangle$,

$$\langle T\rangle=W_0-2W, \qquad (48)$$

and

$$W_0=-\alpha^2/2n^2,\quad W=-\alpha^2/2n^{*2}, \qquad (49)$$

where W_0 is the hydrogenic binding energy, and the effective principal quantum number n^* for the alkalis is taken from experiment,[13] yields

$$(\Delta g/2)_+=\frac{5.33}{12}(1-C)(Z-1)\left(\frac{3}{n^{*2}}-\frac{1}{n^2}\right)\times 10^{-5}, \qquad (50)$$

$$(\Delta g/2)_M=-\frac{5.33}{3}\left(\frac{2}{n^{*2}}-\frac{1}{n^2}\right)\times 10^{-5}, \qquad (51)$$

$$\tfrac{1}{2}(\Delta g/2)_L=-\frac{5.33}{12}\left(\frac{1}{n^{*2}}-\frac{1}{n^2}\right)\times 10^{-5}, \qquad (52)$$

and the total $\alpha^2\mu_0H$ contribution (37), exclusive of self-radiative effects, is

$$\Delta g/2=(\Delta g/2)_+ + (\Delta g/2)_M+\tfrac{1}{2}(\Delta g/2)_L. \qquad (53)$$

The numerical results for hydrogen and the alkalis are shown in Table I. It is seen that $[\Delta g/2-(\Delta g/2)_{\mathrm{Na}}]$ is of the order of magnitude of Kusch and Taub's results (1). On the other hand $[(\Delta g/2)_{\mathrm{K}}-(\Delta g/2)_{\mathrm{H}}]=6.7\times 10^{-5}$ is about four times larger than Franken and Koenig's results (2). Also a steeper rise with Z might have been expected from the analogy with fine structure. The large positive contribution of $(\Delta g/2)_+$ is seen to arise from the low value of C, Eq. (43), which corresponds to small shielding of the nuclear charge by the core electrons in the spin-orbit type term (28).

^2P STATES

The following measured g_J ratios are given by Kusch and Foley[14] and by Mann and Kusch:[15]

$$g_J(\mathrm{Ga}\ ^2P_{\frac{3}{2}})/g_J(\mathrm{Ga}\ ^2P_{\frac{1}{2}})=2(1.00172\pm 6\times 10^{-5}), \qquad (54)$$

$$g_J(\mathrm{In}\ ^2P_{\frac{3}{2}})/g_J(\mathrm{In}\ ^2P_{\frac{1}{2}})=2(1.00200\pm 6\times 10^{-5}), \qquad (55)$$

$$g_J(\mathrm{Na}\ ^2S_{\frac{1}{2}})/g_J(\mathrm{Ga}\ ^2P_{\frac{1}{2}})=3(1.00242\pm 6\times 10^{-5}), \qquad (56)$$

$$g_J(\mathrm{Na}\ ^2S_{\frac{1}{2}})/g_J(\mathrm{In}\ ^2P_{\frac{1}{2}})=3(1.00243\pm 10\times 10^{-5}). \qquad (57)$$

From these by use of (M = magnetic quantum number),

$$\begin{aligned} g_J&=\Delta E_H/M\mu_0H=(\Delta E_N+\Delta E_{RSBC})/M\mu_0H\\ &=\alpha_Lg_L+\alpha_Sg_S+2(\Delta g/2)_{RSBC}, \end{aligned} \qquad (58)$$

and, subtracting off the theoretical self-radiative contributions as in reference 14, by

$$g_L=1,\quad g_S=2(1+\delta_S)=2(1.0011454),$$

$$\alpha_L=2/3,\quad 4/3,\quad 0,$$

$$\alpha_S=1/3,\quad -1/3,\quad 1,$$

for

$$^2P_{\frac{3}{2}},\quad ^2P_{\frac{1}{2}},\quad ^2S_{\frac{1}{2}},\quad \text{respectively,}$$

there remains to be explained

$$[\tfrac{3}{2}(\Delta g/2)(\mathrm{Ga}\ ^2P_{\frac{3}{2}})-3(\Delta g/2)(\mathrm{Ga}\ ^2P_{\frac{1}{2}})]_{RSBC}=(0\pm 6)10^{-5}, \qquad (59)$$

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[13] Reference 12, p. 143.

[14] P. Kusch and H. M. Foley, Phys. Rev. **74**, 250 (1948).

[15] A. K. Mann and P. Kusch, Phys. Rev. **77**, 435 (1950).

$$[\tfrac{3}{2}(\Delta g/2)(\mathrm{In}\ {}^2P_{\frac{3}{2}})-3(\Delta g/2)(\mathrm{In}\ {}^2P_{\frac{1}{2}})]_{RSBC} = (28\pm 6)10^{-5}, \qquad (60)$$

$$[(\Delta g/2)(\mathrm{Na}\ {}^2S_{\frac{1}{2}})-3(\Delta g/2)(\mathrm{Ga}\ {}^2P_{\frac{1}{2}})]_{RSBC} = (13\pm 6)10^{-5}, \qquad (61)$$

$$[(\Delta g/2)(\mathrm{Na}\ {}^2S_{\frac{1}{2}})-3(\Delta g/2)(\mathrm{In}\ {}^2P_{\frac{1}{2}})]_{RSBC} = (14\pm 10)10^{-5}, \qquad (62)$$

in which the experimental results on the right are to be accounted for in terms of the theoretical contributions indicated on the left by subscripts R, S, B, C denoting respectively the "relativistic increase of mass," "spin," "Breit interaction," and "configuration mixing" contributions. Contributions R and B are neglected as being $\lesssim 1\times 10^{-5}$. (Moreover, as $(\Delta g/2)_R$ is by (27) proportional to g_J, Eqs. (54) to (62) will contain approximately equal and opposite contributions from $(\Delta g/2)_R$ on the left-hand sides.) Also, the contributions of Na ${}^2S_{\frac{1}{2}}$ are neglected[1,2] as being $\lesssim 2\times 10^{-5}$. Contribution C is considered by Phillips[3] to be not negligible but also probably insufficiently large to account for all of (59) to (62). For the present approximate purposes it is not considered further.

Contribution S remains to be discussed. With the approximations mentioned, and substituting (61) and (62) into (59) and (60), there results:

$$(\Delta g/2)_S(\mathrm{Ga}\ {}^2P_{\frac{3}{2}}) = (-8.7\pm 6)10^{-5}, \qquad (63)$$

$$(\Delta g/2)_S(\mathrm{Ga}\ {}^2P_{\frac{1}{2}}) = (-4.3\pm 2)10^{-5}, \qquad (64)$$

$$(\Delta g/2)_S(\mathrm{In}\ {}^2P_{\frac{3}{2}}) = (9.3\pm 8)10^{-5}, \qquad (65)$$

$$(\Delta g/2)_S(\mathrm{In}\ {}^2P_{\frac{1}{2}}) = (-4.7\pm 3)10^{-5}. \qquad (66)$$

In the one-electron hydrogenic case Margenau's[5] theoretical results give, analogously to fine structure as previously mentioned, $(\Delta g/2)_S$ negative in $j=l-\frac{1}{2}$ states, $(\Delta g/2)_S$ positive in $j=l+\frac{1}{2}$ states, and, independently of principal quantum number n,

$$-(\Delta g/2)_S({}^2P_{\frac{1}{2}})/(\Delta g/2)_S({}^2P_{\frac{3}{2}}) = 5, \qquad (67)$$

$$(\Delta g/2)_S({}^2S_{\frac{1}{2}})/(\Delta g/2)_S({}^2P_{\frac{3}{2}}) = 5/3. \qquad (68)$$

Assume that these results apply qualitatively to the closed-shell-plus-one-valence-electron ${}^2P$ states under consideration, together with the approximately ten times greater magnitude of the spin contribution relative to that for $Z=1$, for the same range of atomic numbers as previously indicated for ${}^2S_{\frac{1}{2}}$ states. Then the theoretical signs of $(\Delta g/2)_S$ mentioned above agree with (64) and (66) and are not definitely contradicted by (63) and (65). The experimental and theoretical uncertainties are too great to yield a conclusion as regards (67). Finally, the factor 5/3 in (68), which might be expected to be greater in heavy atoms due to increased relative penetration effects (as for fine structure splittings), when applied to (63) and (65) gives values for $(\Delta g/2)_S({}^2S_{\frac{1}{2}})$ not incompatible with the experimental results (1).

Although no great significance can be attached to the present numerical estimates, it may, perhaps, be concluded that the present source should not be overlooked in a quantitative calculation of g values of multi-electron atoms to one part in 10^4 or 10^5. Such a calculation would also be interesting as a test of the theory of fine structure, in view of the similar theoretical origin of $\alpha^2\mu_0 H$ and $\alpha^2\mathrm{Ry}$.

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