Perturbations of Atomic g Values

M. Phillips
Brooklyn College, Brooklyn, New York
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A further investigation of the perturbation by excited core states of gyromagnetic ratios for atoms consisting of a single electron outside closed shells takes account of the spin orbit interaction of the excited core. Although the effect vanishes to lower orders than the fourth, and at least the first term in the expansion of the electrostatic interconfiguration interaction cancels even in that order, there is for alkali atoms a residual correction possibly large enough to account for observed deviations of g values from those expected. Calculations have also been made for ^2P states: The effect in gallium is negligible, but the anomalous observed $g_J(P_{3/2})/g_J(P_{1/2})$ for indium may be at least in part due to perturbations of this kind.

INTRODUCTION

EARLIER discrepancies between experimental and theoretically expected values of atomic gyromagnetic ratios have been mainly resolved by the recognition of the anomalous "intrinsic" magnetic moment of the electron due to radiation reaction.[1-3] More recent[4] calculations of this effect give g for an electron in an s state as $2(1+0.001145)$. Further improvements in experimental technique have made possible a high precision test of the computed value of the anomalous moment,[5] but have also made it necessary to examine all possible factors affecting atomic g values. Variations of these values among the alkalis,[6] and of the ratio of $g(^2P_{3/2})/g(^2P_{1/2})$ for atoms like gallium and indium,[7] while small in comparison to the radiation reaction effect, are not predicted by the quantum electrodynamics. In particular, the observed ground-state g values of cesium and rubidium differ by 13 parts in 10^5 and 5 parts in 10^5, respectively, from that for sodium. The most recently reported g_J value for potassium[8] is greater than the corresponding value for hydrogen by about 1 part in 10^5. The possibility always exists that the atomic gyromagnetic ratio may be affected by interconfiguration interaction with excited core levels for atoms other than hydrogen. The present extension of the perturbation calculation indicates that the perturbations do increase with atomic number, and are of the order of magnitude of the observed discrepancies.

It was previously shown[9] that electrostatic interaction of a one-electron configuration with excited core states, responsible for perturbations of the energies and doublet separations of alkali spectra, does not directly affect the magnetic g values, since it mixes only those states having the same total orbital angular momentum and spin, and therefore the same gyromagnetic ratio.

All other interconfiguration interactions are genuinely small. But the excited core states themselves do not exhibit Russell Saunders coupling for the same reason that the rare gases do not: The parameter comparable in magnitude to the electrostatic energy differences is the spin orbit interaction energy of the incomplete core, which gives rise to separations corresponding to that of a high-lying x-ray doublet. Our purpose here is to extend the perturbation calculation to sufficiently high orders that the effect on the g value of the ground state does not vanish.

A consistent fourth-order perturbation calculation is necessary, since the effect vanishes to lower orders. It will be shown later that is is necessary to write the perturbed ground-state wave function only to second order:

$$\psi=\psi_0+\sum_i \frac{V_{0i}}{E_{0i}}\psi_i+\sum_{i,k}\frac{V_{0i}\xi_{ik}}{E_{0i}E_{0k}}\psi_k. \qquad (1)$$

Here ψ_i and ψ_k represent states of the excited core configuration having the same total angular momentum as the ground state, V_{0i} is the nondiagonal electrostatic interaction mixing the ground state and the ith level of the excited core configuration, and ξ_{ik} is the matrix element of the spin orbit interaction between states i and k. We need to consider only the spin orbit interaction for the "hole" in the core, since that for any external electron is negligibly small. The required g value is then found by evaluating the matrix element of $\mathbf{L}+2\mathbf{S}=\mathbf{J}+\mathbf{S}$ with the use of the wave function ψ appropriate to the particular atom under consideration.

ALKALI GROUND STATES

The excited configurations to be considered in the case of alkali atoms are those in which one electron from the last (closed) p shell is excited to a higher p level, i.e., configurations of the kind $(np)^5(n_0s)(n'p)$, where the total quantum number n is n_0-1, and n' is equal to or greater than n_0, the total quantum number of the s valence electron. The energy denominators corresponding to the excitation of electrons lying deeper in the core are very large, and since parity must be preserved the orbital angular momentum of the excited

[1] P. Kusch and H. M. Foley, Phys. Rev. **72**, 1256 (1947); **73**, 412 (1948).
[2] P. Kusch and H. M. Foley, Phys. Rev. **74**, 250 (1948).
[3] J. Schwinger, Phys. Rev. **73**, 416 (1948).
[4] R. Karplus and N. Kroll, Phys. Rev. **77**, 536 (1950).
[5] Koenig, Prodell, and Kusch, Phys. Rev. **83**, 687 (1951).
[6] P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).
[7] A. K. Mann and P. Kusch, Phys. Rev. **77**, 435 (1950).
[8] P. Franken and S. Koenig, Phys. Rev. **88**, 199 (1952).
[9] M. Phillips, Phys. Rev. **60**, 100 (1941).

electron must remain odd. This does not rule out the possibility of virtual transitions to $n'f$, when such orbits are available, but these terms also have larger excitation energies and their wave functions do not appreciably overlap those of the core. The configuration of interest, indicated above, contains six states with $J=1/2$ and thus possibly are capable of affecting the ground state.

In a consistent perturbation calculation the result is independent of the detailed coupling assumed for the perturbing states, but it is instructive to consider two different coupling schemes. Each of the two schemes makes the states diagonal with respect to one set of parameters at the expense of the other. For example, LS coupling makes both V_{0i} and $\mathbf{J}+\mathbf{S}$ diagonal, but ξ_{ik} connects states within the excited configuration that differ in L and S by at most one unit each. We shall consider this scheme first.

The two external electrons, $n_0 s$ and $n'p$, may be coupled to form the parent states ^1P and ^3P, which when combined with the incomplete core yield $^2S(^1P)$, $^2S(^3P)$, $^2P(^1P)$, $^2P(^3P)$, $^4P(^3P)$, $^4D(^3P)$, all with $J=1/2$. (The parent terms are indicated in parentheses.) The electrostatic interaction V_{0i} with the configuration $(np)^6(n_0 s)$ is then very simple, the sum extending over only the two ^2S states. In fact,

$$\sum_i V_{0i}\psi_i = \tfrac{1}{2}\{(F_0+G_1)\psi_1+\sqrt{3}(F_0-G_1)\psi_2\}, \quad (2)$$

where ψ_1 is the wave function for $^2S(^1P)$ and ψ_2 that for $^2S(^3P)$. The argument of the direct and exchange radial integrals[10] F_0 and G_1 is $(n_0 s, np:n_0 s, n'p)$, i.e., the electrostatic interaction refers to the valence electron and the "jumping" p electron. Turning now to the spin orbit interaction: ξ_{ik} has matrix elements connecting $^2S(^1P)$ with $^2P(^1P)$, and $^2S(^3P)$ with $^2P(^3P)$ and $^4P(^3P)$, thus introducing the possibility of foreign g values. The matrix elements of ξ_{ik} may be computed directly from the state wave functions, or by use of the properties of angular momentum matrices according to rules given by C&S, p. 266 ff. They are

$$(^2S(^1P):\xi:^2P(^1P)) = (1/\sqrt{2})\zeta(np),$$
$$(^2S(^3P):\xi:^2P(^3P)) = (1/3\sqrt{2})\zeta(np), \quad (3)$$
$$(^2S(^3P):\xi:^4P(^3P)) = (2/3)\zeta(np),$$

where $\zeta(np)$ is the spin orbit parameter of the "hole" in the incomplete p shell.

In this coupling scheme it is easy to see that the value of $\mathbf{J}+\mathbf{S}$ for the ground state remains unaffected in first, second, and third order, since $\mathbf{J}$ is the same for all states and the matrix for $\mathbf{S}$ is diagonal. It may also be seen that one obtains the whole of the fourth-order correction from the second-order term in the wave function, for the same reason. In the fourth order the contribution to the gyromagnetic ratio of the ground

state may be found by evaluating

$$\Delta g = \sum_{i,k} \frac{V_{0i}^2\xi_{ik}^2\Delta g_k}{E_{0i}^2 E_{0k}^2}, \quad (4)$$

where the use of $\Delta g_k = g_k - g_0$ automatically takes care of normalization. Since $g_J(^2P_{1/2})=2/3$ and $g_J(^4P_{1/2})=8/3$, and it is permissible to neglect differences in the energy denominators, the substitution of (2) and (3) gives

$$\Delta g = -\tfrac{2}{3}F_0 G_1 \zeta^2(np)/E^4. \quad (5)$$

Whether this correction corresponds to a depression or an elevation of the ground-state g value depends on the relative signs of the direct and exchange electrostatic interaction integrals F_0 and G_1, since both square terms cancel. A knowledge of configuration interaction would be necessary in order to ascertain the values of these integrals directly from spectroscopic data, and even the answer to the question of relative sign cannot be predicted in all cases with absolute certainty. Approximations based on plotting reasonable wave functions for the heavier alkalis, however, indicate that the F_0 and G_1 appearing in (5) are always unlike in sign; and for atoms of lower atomic number, where similar integrals have been evaluated more carefully,[11] the signs have indeed been opposite. It therefore seems safe to conclude that the effect of the perturbation is to raise the ground-state g value by an amount depending on the absolute values of the parameters involved.

With the exception of the electrostatic integrals these parameters may be reliably estimated from spectroscopic data. The energy levels of the rare gas atom having the same electronic configuration as the core of the alkali atom in question yield values of ζ and E, both somewhat too small. The ratio of ζ/E will be appreciably larger for the alkali, however, since ζ varies as the fourth power of the effective nuclear charge and the excitation energy only as Z_{eff}^2. The core doublet separation associated with $\zeta(np)$ increases rapidly with atomic number: $\zeta(np)$ is about 514 cm^{-1} for Ne, 954 for A, 3600 for Kr, and 7100 for Xe. Examination of the data[12] gives a basis for reasonable estimates of ζ/E as follows: 1/200 for Na, 1/70 for K, 1/20 for Rb, and 1/10 for Cs. The excitation potential decreases as one goes to higher atomic number, but so slowly that the ratio ζ/E rises rapidly.

For a rough approximation to the values of F_0 and G_1 one may conclude that the maximum value of F_0 is not likely to be more than one-third to one-half of the average of the diagonal integrals $F_0(np, n_0 s)$ and $F_0(n'p, n_0 s)$, while the exchange integral G_1 could be nearly equal to the corresponding diagonal value for

[10] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 174 ff. This important reference will be referred to hereafter as C&S.

[11] See, e.g., M. Phillips, Phys. Rev. 44, 644 (1933).

[12] C. E. Moore, *Atomic Energy Levels*, Vol. 1, National Bureau of Standards Circular No. 467 (1948), ends with data for $Z=23$. For higher Z no papers consulted show surprising differences from relevant data available systemmatically in R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

electrons within either configuration. The analysis of appropriate spectra for values of these last integrals has been made.[13] Their trend with atomic number, relative to the excitation energy, is opposite to that of ζ/E, decreasing as one goes to heavier atoms, although slowly. For Cs the F_0G_1/E^2 appearing in (5) could hardly be greater than 1/200 for the lowest value of n', and would fall off rather rapidly with increasing n'. Since E increases only very slowly with n', however, and ζ is constant, it is probable that the contributions from all higher excited p orbits amount to at least as much as the first, so that the total Δg for Cs may be as much as 6 or 8 parts in 10^5. It is not possible to rule out surprisingly large F_0 and G_1, and thus the possibility exists that the observed discrepancy may be entirely due to this effect.

For potassium, on the other hand, ζ^2/E^2 is already small, 2 parts in 10,000. If F_0G_1/E^2 is fifty times larger for the first excited p orbit, which seems a reasonable estimate from spectroscopic data and known configuration interactions in this neighborhood, g would be affected by only a few parts in 10^6. This estimate could easily be too small, but more than one part in 10^5 seems out of the question. For sodium the effect of perturbations is still smaller than for potassium. For rubidium we would expect about one-third the perturbation found in cesium.

The whole problem may be set up quite differently, by considering the j of the incomplete shell as a good quantum member and coupling this $j=1/2, 3/2$ separately to the external $(n_0s)(n'p)$ combination. This scheme is a closer approximation to the actual physical situation, especially for atoms of high atomic number, where the states of any configuration involving an incomplete shell are grouped in two sets corresponding to the two members of the parent doublet. The calculation has been carried out in this way, to check the method. The complications which arise are due to the fact that while $\xi(np)$ is now diagonal all six $J=1/2$ states are mixed with the zero-order ground state by the electrostatic interaction, and cross terms in $\mathbf{J+S}$ arise. The final answer is just that given by (5).

PERTURBATIONS OF ^2P g VALUES

For atoms like gallium, indium, and thallium, with ground-state configuration $(n_0s)^2(n_0p)$, virtual excitation of the highest filled d shell gives most promise of affecting the g values associated with the two members of the ^2P. The excitation energy of any deep-lying p electron is very large, and s electron excitation does not affect the magnetic moment because it furnishes no parent doublet. The parity limitation permits excitation of a d electron to higher d and unfilled s orbits, but investigation shows so much angular interference in the computation of the electrostatic matrix elements

[13] E. U. Condon and G. H. Shortley, Phys. Rev. 35, 1342 (1930).

for the latter case that it suffices to consider excited configurations $(nd)^9(n_0p)(n'd)$, $n' \geqslant n_0$.

Again the assumption of LS coupling provides the simplest method of describing the perturbation. Six ^2P states occur in the excited configuration, which may be ascribed to parent terms of the $(n_0p)(n'd)$ combination, ^1P, ^3P, ^1D, ^3D, ^1F, ^3F, coupled with the incomplete core shell $(nd)^9$. The wave function for the ground state of the unexcited atom can be represented as a linear combination of the wave functions for these six states if n' is read as n, a device that simplifies the computation of the electrostatic interaction energy:

$$\psi_0 = \frac{1}{2\sqrt{30}}\{-\sqrt{6}\psi(^1P) - 3\sqrt{2}\psi(^3P) + \sqrt{10}\psi(^1D)$$

$$+ \sqrt{30}\psi(^3D) + \sqrt{14}\psi(^1F) + \sqrt{42}\psi(^3F)\}. \quad (6)$$

Here each ψ is formally the wave function associated with the particular ^2P level of the excited state for which the two-electron parent term is indicated in parentheses. The cancellation of zero-order single electron product functions (antisymmetrized) is such that the sum is compatible with the exclusion principle applied to a closed d shell. The electrostatic interaction between the ground state and any one ^2P of the excited configuration has the same form as that of its $(n_0p)(n'd)$ parent, since just these two electrons are involved, although in the interpretation of each radial integral it must be remembered that the d electron is not diagonal with respect to its total quantum number. There are four terms in the expansion of the electrostatic interaction, but their coefficients may be readily calculated and are, in fact, just those given on p. 200, C&S. These expressions must be multiplied by the appropriate coefficient in ψ_0 as given by (6) to yield a particular V_{0i}.

All that is now needed is the matrix of ξ_{ik} connecting the ^2P states of the excited configuration with neighboring states of different L and S. In this calculation the two terms of the doublet must be considered separately: For $^2P_{3/2}$ there are in all thirteen combining states, whereas only eight states combine with various $^2P_{1/2}$ levels. The values of these matrix elements are given in the appendix, together with the substitution in the expression for Δg.

The final result shows that the largest terms cancel much more completely for the ground state $^2P_{1/2}$ than for the alkali atom ground states. Not only does the coefficient of F_0^2 vanish, but so do those of all cross terms involving F_0. The leading term that remains, in G_1^2, has a negative sign, so that $g_J(^2P_{1/2})$ may be very slightly depressed. In considering G_1, F_2, etc., it must be noted that these symbols already include the denominators resulting from the angular integration, i.e., $G_1 = G^1/15$, $F_2 = F^2/35$, $G_3 = G^3/245$, where G^1, F^2 and G^3 are radial integrals. For the $^2F_{3/2}$ level, however,

$F_0{}^2$ and F_0F_2 have zero coefficients, but F_0G_1 does not:

$$g_J(^2P_{3/2}) = -\tfrac{3}{5}\,F_0G_1\zeta^2(nd)/E^4, \qquad (7)$$

in addition to smaller terms. It thus appears that the ratio $g_J(^2P_{3/2})/g_J(^2P_{1/2})$ may be perceptibly perturbed as a result of the perturbation of $g_J(^2P_{3/2})$.

Considerations analogous to those for alkali atoms lead only to very rough quantitative estimates of the effects of these perturbations. The positions of the nodes in the radial wave functions make it highly probable that F_0 and G_1 are opposite in sign, so that the value of $g_J(^2P_{3/2})$ is increased. The spectroscopic data on neighboring metallic ions show that ζ/E again increases markedly with atomic number. (ζ is 2/5 the energy separation of the ^2D associated with $(nd)^9$.) Reasonable estimates $(\zeta/E)^2$ are $16/10^4$ for gallium, $4/100$ for indium, $12/100$ for thallium. Numerical values of the electrostatic energy parameters, however, are considerably less certain than in the case of the alkalis: The related spectra are much more complicated, with repeated spectral terms of the same character, so that identification of levels with those calculated is almost impossible. In other words, not even the diagonal electrostatic integrals are well known. Nevertheless, it is apparent that the effect would be too small to observe easily in gallium. While the perturbation is greater for indium, the observed discrepancy in the indium ratio seems somewhat too large to be accounted for in this way, if the parameters vary smoothly with atomic number. A check would be furnished by measurements on the thallium ratio, where Δg given by (7) or (10) should be about five times as great as in indium.

APPENDIX

The matrix elements of the incomplete core spin orbit interaction between ^2P states of the excited configuration $(nd)^9(n_0p)(n'd)$ and other states of the same configuration are given below. The $(n_0p)(n'd)$ parent term must be the same for two states in order that ξ_{ik} not vanish, and it is indicated only in the specification of ^2P. The corresponding Δg_k appears on the right.

		Δg_k
$J = 3/2$	$(^2P(^1P):\xi:^2D) = \tfrac{3}{4}\zeta(nd),$	$-8/15$
	$(^2P(^1D):\xi:^2D) = \tfrac{1}{4}\sqrt{21}$	$-8/15$
	$(^2P(^1F):\xi:^2D) = \sqrt{(3/2)}$	$-8/15$
	$(^2P(^3P):\xi:^2D) = \tfrac{1}{4}$	$-8/15$
	$(^2P(^3P):\xi:^4P) = \tfrac{1}{2}\sqrt{5}$	$6/15$
	$(^2P(^3P):\xi:^4D) = \tfrac{1}{2}$	$-2/15$
	$(^2P(^3P):\xi:^2D) = \tfrac{1}{4}\sqrt{(7/3)}$	$-8/15$
	$(^2P(^3D):\xi:^4S) = \sqrt{(2/3)}$	$2/3$
	$(^2P(^3D):\xi:^4P) = \tfrac{1}{6}\sqrt{5}$	$6/15$
	$(^2P(^3D):\xi:^4D) = \tfrac{1}{2}\sqrt{(7/3)}$	$-2/15$
	$(^2P(^3F):\xi:^2D) = 1/\sqrt{6}$	$-8/15$
	$(^2P(^3F):\xi:^4P) = -\tfrac{1}{3}\sqrt{5}$	$6/15$
	$(^2P(^3F):\xi:^4D) = \sqrt{(2/3)}$	$-2/15$
$J = 1/2$	$(^2P(^1D):\xi:^2S) = \sqrt{(3/2)}\zeta(nd)$	$4/3$
	$(^2P(^3P):\xi:^4P) = -1/\sqrt{2}$	2
	$(^2P(^3P):\xi:^4D) = 1/\sqrt{2}$	$-2/3$
	$(^2P(^3D):\xi:^2S) = -1/\sqrt{6}$	$4/3$
	$(^2P(^3D):\xi:^4P) = -1/3\sqrt{2}$	2
	$(^2P(^3D):\xi:^4D) = \sqrt{(7/6)}$	$-2/3$
	$(^2P(^3F):\xi:^4P) = \tfrac{1}{3}\sqrt{2}$	2
	$(^2P(^3F):\xi:^4D) = 2/\sqrt{3}$	$-2/3$

With these values and those for V_{0i} the perturbation of g_J is immediately available.

$$\Delta g_J(^2P_{1/2}) = (-5G_1{}^2 + 14F_2G_1)\zeta^2/E^4, \qquad (8)$$

plus terms in $F_2{}^2$ and smaller. To a similar approximation

$$\Delta g_J(^2P_{3/2}) = (-0.6F_0G_1 - 2.5G_1{}^2)\zeta^2/E^4. \qquad (9)$$

The first two terms in the correction of the ratio are

$$\Delta g_J(^2P_{3/2})/g_J(^2P_{1/2}) = (-0.6F_0G_1 + 2.5G_1{}^2)\zeta^2/E^4. \qquad (10)$$