PHYSICAL REVIEW VOLUME 76, NUMBER 12 DECEMBER 15, 1949

The Effect of Nuclear Motion on Atomic Magnetic Moments

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(Received August 18, 1949)

The effect of the finite mass of the nucleus on the Zeeman pattern of multi-electron atoms is investigated. This effect consists of two parts, one due to the motion of the core and nucleus about the center of mass, the other an exchange phenomenon between the electrons themselves. Both are of order m/M, where M is the mass of the nucleus.

THE effect of the finite mass of the nucleus on the Zeeman pattern of multi-electron atoms is small, but with the increasingly high precision attainable in the measurement of magnetic moments[1] it may become quantitatively significant. While the apparent anomalies of the g ratios in atoms consisting of one electron outside closed shells are qualitatively understood in terms of the "intrinsic" moment of the electron, there remain small discrepancies between theory and experiment. The present consideration does little or nothing to resolve these discrepancies, but it seems desirable to investigate all relevant factors which might effect the interpretation of the experimental results.

To take account of the motion of all the charged particles composing an atom let $\mathbf{r}$ and $\mathbf{r}_i$ be the position vectors of the nucleus and electrons with respect to a fixed point. The total kinetic energy is then

$$T_0=(1/2M)\mathbf{p}^2+(1/2m)\textstyle\sum_i \mathbf{p}_i^2$$

where $\mathbf{p}$ and $\mathbf{p}_i$ are the momenta conjugate to $\mathbf{r}$ and $\mathbf{r}_i$. It is in this system of coordinates that a constant field $\mathbf{H}$ is represented by the vector potential $\mathbf{A}=\frac{1}{2}\mathbf{H}\times\mathbf{r}$, and can be introduced into the Hamiltonian by the well-known substitution $\mathbf{p}\rightarrow\mathbf{p}-Ze\mathbf{A}/c$ and $p_i\rightarrow\mathbf{p}_i+e\mathbf{A}_i/c$. To first order in H,

$$\begin{aligned}T=T_0+T_H=&(1/2M)(\mathbf{p}^2-(2Ze/c)\mathbf{p}\cdot\mathbf{A})\\&+(1/2m)\textstyle\sum_i[\mathbf{p}_i^2+(2e/c)\mathbf{p}_i\cdot\mathbf{A}_i]\end{aligned}$$

and

$$T_H=-(Ze/2Mc)\mathbf{H}\cdot\mathbf{r}\times\mathbf{p}+(e/2mc)\textstyle\sum_i\mathbf{H}\cdot\mathbf{r}_i\times\mathbf{p}_i.$$

Transforming to the Hamiltonian operator in the usual way, $\mathbf{p}\rightarrow(\hbar/i)$grad, and assuming that the magnetic field is directed along the z axis,

$$\begin{aligned}T_H=(eH/2c)(\hbar/i)\{&(-Z/M)(\mathbf{r}\times\nabla_r)_z\\&+(1/m)\textstyle\sum_i(\mathbf{r}_i\times\nabla_{ri})_z\}.\end{aligned}$$

If we now introduce the coordinate vector $\mathbf{R}$ of the center of mass, and the relative coordinates $\mathbf{s}_i$ of the electrons with respect to the nucleus,

$$\mathbf{s}_i=\mathbf{r}_i-\mathbf{r},\quad (m+Mm)\mathbf{R}=M\mathbf{r}+m\textstyle\sum\mathbf{r}_i,$$

that portion of the Hamiltonian operator which varies as the first power of H becomes:

$$\begin{aligned}T_H=\frac{eH}{2c}\frac{\hbar}{i}\bigg\{&-\frac{Z}{M}\bigg[\bigg(\mathbf{R}-\frac{m}{M+Nm}\sum_i\mathbf{s}_i\bigg)\\&\times\bigg(\frac{M}{M+Nm}\nabla_R-\sum_i\nabla_{s_i}\bigg)\bigg]_z\\&+\frac{1}{m}\sum_i\bigg[\bigg(\mathbf{R}+\frac{M+(N-1)m}{M+Nm}\mathbf{s}_i-\frac{m}{M+Nm}\sum_{j\neq i}\mathbf{s}_j\bigg)\\&\times\bigg(\frac{m}{M+Nm}\nabla_R+\nabla_{s_i}\bigg)\bigg]_z\bigg\}.\end{aligned}$$

It is legitimate to neglect the motion of the center of mass, so that $\mathbf{R}$ and the momentum conjugate to $\mathbf{R}$ may be set equal to zero. The terms of interest are therefore:

$$\begin{aligned}T_H=\frac{eH}{2c}\frac{\hbar}{i}\bigg\{&\bigg(-\frac{Z}{M}\frac{m}{M+Nm}+\frac{M+(N-1)m}{M+Nm}\bigg)\\&\times\sum_i(\mathbf{s}_i\times\nabla_{s_i})_z-\frac{1}{M+Nm}\bigg(\frac{Zm}{M}+1\bigg)\\&\times\sum_{j\neq i}[(\mathbf{s}_j+\nabla_{s_i})_z+(\mathbf{s}_i\times\nabla_{s_j})_z]\bigg\}.\end{aligned}$$

For a neutral atom, in which N, the number of electrons, is equal to Z, the nuclear charge number, this simplifies to the expression:

$$\begin{aligned}T_H=\frac{eH}{2mc}\frac{\hbar}{i}\bigg\{&\bigg(1-\frac{m}{M}\bigg)\sum_i(\mathbf{s}_i\times\nabla_{s_i})_z\\&-\frac{m}{M}\sum_{j\neq i}[(\mathbf{s}_j\times\nabla_{s_i})_z+(\mathbf{s}_i\times\nabla_{s_j})_z]\bigg\}\\=&\,T_{H0}+T_{H1}.\end{aligned}$$

The first term, T_{H0}, gives rise to the well-known eigenvalue l_z for each electron, although it is to be noticed that the factor $(1-m/M)$ enters. The second term, T_{H1}, is analogous to the "specific isotope effect"

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

in atomic spectra,[2] and has already been mentioned in connection with atomic g values.[3]

The matrix elements of $(s_i \times \nabla s_j)_z$ may be readily evaluated in terms of radial integrals if all quantities are expressed in polar coordinates and determinantal electronic wave functions are used. Only exchange integrals will contribute for any given configuration, and these always enter with a negative sign because of the antisymmetry of the atomic wave functions. Those pairs of electrons will interact which have the same spin, opposite individual parity, and m_l values differing by ± 1. This means, for example, that a p valence electron in an atom such as gallium or indium will interact with one s electron in each closed s shell, and two d electrons in each closed d shell. (The sum of all such interactions between electrons within closed shells is zero, just as T_{H_0} is zero in that case.)

For the normal configuration of an atom like gallium or indium, consisting of an n_0p valence electron outside closed s and d shells, the total contribution due to interaction with these shells is

$$T_{H_1} = \frac{eHh}{2mc}\frac{m}{M}\frac{2}{3}\Bigg\{ \sum_{n\geq 1} \int_0^\infty R(ns)rR(n_0p)r^2dr \times \int_0^\infty R(n_0p)\frac{\partial R(ns)}{\partial r}r^2dr - \sum_{n\geq 3}\int_0^\infty R(nd)rR(n_0p)r^2dr\left[\int R(n_0p)\frac{\partial R(nd)}{\partial n}r^2dr + 3\int_0^\infty R(n_0p)\frac{1}{r}R(nd)r^2dr\right]\Bigg\}.$$

Here r refers to the polar coordinates, r, θ, ϕ, relative to the nucleus, and R is the appropriate single electron radial wave function. The summation, of course, extends only over closed shells.

The radial integrals in the expression above are elementary in terms of hydrogenic wave functions, but the results of such computations can serve only as a very rough guide, since the penetrating p orbit and all the core orbits involved are distorted by the charge distribution of the core itself. The matrix elements of r are relatively well known, because of their relation to the intensities of radiation from the ionized atom. The integrals involving $1/r$ and the derivatives of the wave functions, however, are difficult to estimate. The main contribution to these integrals comes from inside the core, where the distribution of nodes is very critical. The use of hydrogenic wave functions and the same screening constant for the n_0s and n_0p electrons causes the interaction with the closed n_0s shell to be exactly zero, although the interaction with the inner s shells does not vanish. Also, in the case of the normal $4p$ state of gallium, the first term of the interaction with the $3d$ shell vanishes, since the derivative of $R(3d)$ is a constant times $R(3p)$. The net result, using hydrogenic wave functions for gallium, is that T_{H_1} is somewhat less than, although of the same order as, the correction for the motion of the core as a whole, i.e., the sum of the radial integrals in the bracket above is slightly less than unity. There is no obvious reason why improved wave functions should not give an answer several times as great as this, although not of a higher order. A very similar result is obtained for indium: again the contribution of the overlapping s shell is zero, although there is a non-vanishing interaction with deeper s shells and both d shells.

It would be routine, although tedious, to evaluate T_{H_1} using numerically integrated wave functions with something like a self-consistent field. At present the experimental precision does not seem to warrant such a calculation, especially since the relativistic correction is presumably somewhat more important.

APPENDIX

To write the matrix elements in polar coordinates:

$$(s_i \times \nabla s_j)_z = \left(x_i\frac{\partial}{\partial y_j} - y_i\frac{\partial}{\partial x_j}\right) = \frac{i}{2}(\eta_{ij}\bar{\zeta} - \bar{\eta}_i\zeta_j) = G(i, j),$$

where

$$\eta_i = x_i + iy_j = r_i \sin\theta_i e^{i\phi_i}$$

and

$$\zeta_j = \frac{\partial}{\partial x_j} + i\frac{\partial}{\partial y_j} = \sin\theta_j e^{i\phi_j}\left(\frac{\partial}{\partial r_j} + \frac{\cos\theta_j}{r_j \sin\theta_j}\frac{\partial}{\partial\theta_j} + \frac{i}{r_j \sin^2\theta_j}\frac{\partial}{\partial\varphi_j}\right).$$

The integrals to be evaluated are then:

$$-\int d\tau_1 \int d\tau_2 \{\bar{v}(1)\bar{u}_p(2)Gu_p(1)v(2) + \bar{v}(2)\bar{u}_p(1)Gu_p(2)v(1)\}.$$

Here u_p is the wave function of the valence electron, and v is the single particle function for the interacting core electron. When these wave functions are introduced the angular integrals are elementary, and the matrix element of $(s_i \times \nabla s_j)_z + (s_j \times \nabla s_i)_z$ involving any s shell is

$$-\frac{i}{3}\int_0^\infty R(ns)rR(n_0p)r^2dr\left[\int_0^\infty R(ns)\frac{\partial R}{\partial r}(n_0p)r^2dr - \int_0^\infty R(n_0p)\frac{\partial R(ns)}{dr}r^2dr + 2\int_0^\infty R(ns)\frac{1}{r}R(n_0p)r^2dr\right]$$

$$= +\frac{2i}{3}\int_0^\infty R(ns)rR(n_0p)r^2dr\int_0^\infty R(n_0p)\frac{\partial R(ns)}{\partial r}r^2dr.$$

The analogous result for the interacting d electron with azimuthal quantum number equal to zero is

$$\frac{2i}{15}\int_0^\infty R(n_0p)rR(nd)r^2dr\left[\int_0^\infty R(n_0p)\frac{\partial R(nd)}{dr}r^2dr + 3\int_0^\infty R(n_0p)\frac{1}{r}R(nd)r^2dr\right].$$

The interaction with the d electron having azimuthal quantum number 2 gives

$$-\frac{4i}{5}\int_0^\infty R(n_0p)rR(nd)r^2dr\left[\int R(n_0p)\frac{\partial R(nd)}{\partial r}r^2dr + 3\int_0^\infty R(n_0p)\frac{1}{r}R(nd)r^2dr\right].$$

The final expression for T_{H_1} in the main body of the paper is just the sum of all such matrix elements, multiplied by the constants in the Hamiltonian.

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[2] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

[3] M. Phillips, Phys. Rev. **60**, 100 (1941).