

Magnetism and the structure of atoms*

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The modern development of the theory of atomic magnetism without doubt merits the closest attention. The past few years have brought to the quantum theory a number of very major successes in this area. The questions of atomic magnetism have proved to be intimately bound up with questions of the complex structure of the spectral lines, the internal structure of the atom, and so forth. It is particularly interesting that the various characteristic aspects of the entire present-day formulation of quantum theory as a whole is reflected with unusual clarity in the theory of magnetism. One must acknowledge, on the one hand, the striking success of ideas that are simple to the point of naivete, and on the other hand the accumulation of annoying *internal* inconsistencies. These contradictions, which have their roots in the application of the laws of classical physics to the stationary states of the atom, are perhaps nowhere manifested so clearly and distinctly as in the field we shall discuss. For this reason the further development of the quantum theory of magnetism promises to be particularly fruitful.

This theory has grown so much that no systematic account of the related problems has been published. The present paper will be focused mainly on the question of the *net magnetic moment of the atom as a whole*; questions about the *intra-atomic* magnetism, which are so important for the theory of spectra, will be touched on only to the extent necessary to support the overall picture. Of course, ferromagnetic phenomena will be omitted entirely, since they are rooted in the interaction between atoms.

1. THE LANGENVIN THEORY AND THE WEISS MAGNETON

Before turning to a discussion of present-day theories of magnetism, we should recall the experimental basis of the study of atomic magnetism.

Except for new spectroscopic methods, a discussion of which would be premature, there is only one means of determining the magnitude of the magnetic moment of paramagnetic atoms; this is the method based on the kinetic theory of Langenvin.¹⁾ In view of the extreme importance of this theory, let us recall briefly its principal features.

Let us consider a paramagnetic gas whose molecules have a magnetic moment m . In the absence of an external magnetic field the gas molecules are oriented in a disordered manner. A magnetic field tends to align the magnetic axes of the molecules along the direction of the magnetic field, but the thermal motion opposes this alignment. As a result, a steady state is established in which, according to the well-known theorem of statistical mechanics, the distribution of the axes over the various directions is given by the Boltzmann formula

$$dn = ce^{-P/kT} d\omega.$$

Here dn is the number of molecules per mole whose axes fall within the solid angle $d\omega$; P is the potential energy corresponding to this orientation of the molecule, k is Boltzmann's constant, and T is the absolute temperature. If the angle between the magnetic axis of a molecule and the direction of the magnetic field H is φ , then $P = -mH \cos \varphi$.

Introducing the notation

$$a = \frac{mH}{kT},$$

we find

$$dn = ce^{a \cos \varphi} d\omega.$$

In all cases of present interest a is small, and therefore the quantity $e^{a \cos \varphi}$ can be expanded in a series, with only the first terms of the series retained:

$$dn = c(1 + a \cos \varphi) d\omega.$$

The coefficient of proportionality c is determined by the condition that the total number of molecules in a mole must equal Avogadro's number N . Carrying out the calculations, we find that $c = N/4\pi$, and therefore

$$dn = \frac{N}{4\pi} (1 + a \cos \varphi) d\omega.$$

The total magnetic moment of dn molecules is mdn , to which corresponds the component dG of the magnetization in the direction of the field H

$$dG = m \cos \varphi dn = \frac{Nm}{4\pi} \cos \varphi (1 + a \cos \varphi) d\omega.$$

Integrating over all possible directions of the axes, we obtain the total magnetization of one mole of gas

$$\begin{aligned} G &= \frac{Nm}{4\pi} \int (\cos \varphi + a \cos^2 \varphi) d\omega \\ &= \frac{Nma}{4\pi} \int \cos^2 \varphi d\omega = Nma \overline{\cos^2 \varphi}. \end{aligned}$$

Here $\overline{\cos^2 \varphi}$ as usual, stands for the average value of $\cos^2 \varphi$ over all possible orientations of the molecule

$$\begin{aligned} \overline{\cos^2 \varphi} &= \frac{1}{4\pi} \int \cos^2 \varphi d\omega \\ &= \frac{1}{4\pi} \int \int \cos^2 \varphi \cdot \sin \varphi d\lambda d\varphi = \frac{1}{3}. \end{aligned}$$

However, we shall not yet insert this numerical value into the previous formula, but only the value of the quantity a . We obtain

$$G = \frac{Nm^2H}{kT} \cos^2 \varphi.$$

Dividing both sides of this equation by H , we obtain an expression for the magnetic susceptibility (per mole)

$$\chi = \frac{G}{H} = \frac{Nm^2}{kT} \cos^2 \varphi.$$

Multiplying the top and bottom of the fraction by Avogadro's number N and recalling that $Nk=R$, where R is the universal gas constant, and also introducing the notation $Nm=M$, we obtain finally

$$\chi = \frac{M^2}{RT} \cos^2 \varphi, \quad \cos^2 \varphi = \frac{1}{3}. \quad (1)$$

This is the final form of the Langenvin formula for the case $a \ll 1$. This theoretical formula is in complete agreement with the previously obtained empirical formula of P. Curie

$$\chi = \frac{C}{T}, \quad C = \text{const}, \quad (2)$$

which describes very well the temperature dependence of the magnetic susceptibility of a large number of paramagnetic substances. A comparison of the right-hand sides of these formulas yields

$$C = \frac{M^2}{R} \cos^2 \varphi,$$

from which we have

$$M = \sqrt{\frac{RC}{\cos^2 \varphi}}. \quad (3)$$

Now setting $\cos^2 \varphi = 1/3$, we obtain finally

$$M = \sqrt{3RC}. \quad (3a)$$

Since the Curie constant C is determined from experimental data, this formula can be used to determine M .

This theory of Langenvin applies to paramagnetic gases; for paramagnetic solids and liquids the temperature dependence is no longer expressed by the Curie formula (2), but by the more complicated formula with two constants

$$\chi = \frac{C}{T - \Theta}, \quad C = \text{const}, \quad \Theta = \text{const}. \quad (2a)$$

Weiss¹ was able to give a theoretical interpretation of this more complicated formula. We assume that during the magnetization an internal magnetic field H_i is created, which is proportional to the magnetization, $H_i = \lambda G$, and that this internal field in turn acts to orient the molecules of the material. That is, the magnetic interaction between the molecules is taken into account. Then it is necessary to make the appropriate corrections to the expression for P and a . Obviously, in this case

$$a = \frac{m(H + H_i)}{kT} = \frac{m(H + \lambda G)}{kT}.$$

Repeating the previous line of reasoning, we arrive at the final formula of type (2a):

$$\chi = \frac{C}{T - \lambda C}$$

where, as before

$$C = \frac{M^2}{R} \cos^2 \varphi. \quad (3)$$

Thus formula (3) turns out to be applicable to all paramagnetic substances, regardless of their state of aggregation.

Weiss applied this formula to a large number of paramagnetic materials and arrived at the conclusion that the magnetic moments of the various molecules are almost always related by the ratio of whole numbers. In other words, Weiss found that the magnetic moment of a molecule is always an integral multiple of some elementary magnetic moment, which, by analogy with the electron, was called the magneton.²⁾ The value of this elementary magnetic moment m_0 turned out to be $18.6 \cdot 10^{-22}$ cgs units. It is usual, however, not to use m_0 , but the quantity $M_0 = Nm_0 = 1123.5 \text{ G} \cdot \text{cm}$, i.e., the magnetic moment per mole of the substance.

As is well-known, the magnetic properties of chemical compounds are additive. In verifying this rule, however, it is necessary to take into account the state of ionization of the atoms, which has a decisive influence on their magnetic properties. In other words, it is necessary to distinguish the magnetism of neutral atoms from that of the corresponding ions. In return, the magnetic moment of an atom in a given state of ionization is almost wholly independent of the state of aggregation of the material (a solution, a crystalline compound, etc.).

By way of illustration, Table I shows the values of the magnetic moments of the Mn^{II} ion, as determined by various investigators.³⁾ As usual, the Weiss magneton is taken to be the unit of magnetic moment in this table.

One of the foremost specialists in the magnetism of salts, the Spanish physicist P. Cabrera, considers it "almost certain" that the magnetic moment of the Mn^{II} ion is equal to 29.0 magnetons. To the uninitiated, the zero after the decimal point seems premature, to say the least, since the agreement among the various determinations is not sufficient to permit assignments of the decimal places. This example is quite typical of the theory of the Weiss magneton. The correctness of this theory, which states that the magnetic moments of the atoms are equal to an integral number of Weiss magnetons, has many times been called into doubt.⁴⁾ It has been pointed out that its proponents are known to be biased in the deduction of average numbers, and it has also been noted that some atoms and ions have such a large number of magnetons (up to 30), that, given the low accuracy of the experimental data, the difference between such large integral numbers and intermediate fractional numbers is within the experimental error. It is clear that in any case the reality of the Weiss magneton cannot be said to be finally established. It must, however, be recognized that for some materials the measure-

TABLE I.

Compound	Solid Anhydrous Salt	With Water of Crystallization 4H ₂ O	In Aqueous Solution	Investigator
Mn ^{II} SO ₄	29.04(Th) 29.0 29.05(Th)	29.2 O 29.06 (single crystal) F	29.33	Th (Theodorids, 1922) H (Honda, 1914)
Mn ^{II} (NO ₃) ₂	—	—	29.33 C	O (K. Onnes & Oosterhuis, 1913)
Mn ^{II} Cl ₂	28.45(Th) 27.3 H	—	-29.43 C	F (Foex, 1921)
Mn ^{II} O	{ 27.43(Th) 26.43(Th) } 30.2	—	—	C (Cabrera)

ments give numbers of magnetons that are in fact very close to integers. In any case, a great merit of the Weiss theory of the magneton is that it has served as a stimulus to a large number of investigations that have collected a great deal of experimental data.

It is well known that paramagnetism is found almost exclusively in those parts of the Periodic Table where the inner electron layers of the atom undergo rearrangement. These are the triad of elements that include the elements of the eighth group and the elements immediately before those, as well as the rare earth elements. However, only the elements of the iron group from Ti (22) to Ni (28) have been studied with any thoroughness, and therefore in most cases we must henceforth limit the discussion to this group of elements. Table II lists data on the number of magnetons in various ions of this group. For most of them the number of magnetons is taken from the report of Cabrera,² while the data for Mn^{II} and Mn^{III} were taken from the paper of Gerlach.^a Finally, the number of magnetons in V^{II} and V^{III} was determined by Pascal and cited in the present paper following the report of Weiss. The last row of the table gives the range of the various measurements for several ions.

2. THE BOHR MAGNETON

The Weiss "theory of the magneton" is purely empirical. It can be given a theoretical foundation only on the basis of specific ideas on the structure of the atom. The study of atomic structure has made such great advances in the last decade that it would appear that all the prerequisites are now at hand for the theory of atomic magnetism.

First, the work of Einstein and de Haas and of Barnett and their successors has revealed the existence of *magneto-mechanical effects*, that is, the magnetization of ferromagnetic metals and alloys as a result of rapid rotation, and conversely, the appearance of rotational ponderomotive forces during the magnetization of these metals. These experiments provided the long-awaited demonstration of the Amperian theory of molecular currents, and at the present

time it can be regarded as beyond doubt that the magnetism of atoms is due to the motion of electrical particles within the atoms.

On the other hand, the study of Bohr on the structure of atoms has made it possible to calculate *a priori* the actual value of the magnetic moments of atoms, and with almost no additional assumptions to arrive at the concept of the magneton. In other words, the Bohr theory asserts that the atomic moments must be integral multiples of a certain elementary magnetic moment, the magneton. However, despite the qualitative correspondence between the magnetic theories of Bohr and Weiss, there is a great quantitative discrepancy between them: the theoretical unit of magnetism of Bohr, the "Bohr magneton," is five times as large as the empirically determined "Weiss magneton."

The actual calculation of the magnitude of the Bohr magneton presents no difficulties. According to the quantum theory, the angular momentum j of an electron in an atom must be an integral multiple of $h/2\pi$:

$$j = \mu[\mathbf{rv}] = \frac{nh}{2\pi}, \quad n = 1, 2, 3, \dots \quad (4)$$

where μ is the electron mass, \mathbf{r} is its distance from the center of the atom, and \mathbf{v} is its velocity (the square brackets denote the cross product). It is well known that the angular momentum \mathbf{j} is equal to an area-related constant; that is, it is equal to twice the sectorial velocity of the electron multiplied by its mass

$$j = 2\mu \frac{ds}{dt} \quad (5)$$

where s is the area swept out by the radius vector.

On the other hand, in the calculation of the magnetic field of a moving electron we can replace the electron by a loop current i defined by

$$i = \frac{\epsilon}{T}$$

TABLE II.

Identity of Ion	Cr ^{II}	Cr ^{III}	Mn ^{II}	Mn ^{III}	Mn ^{IV}	Fe ^{II}	Fe ^{III}	Co ^{II}	Ni ^{II}	Ti ^{III}	V ^{II}	V ^{III}
Number of Magnetons	24.0	19.0	29.0	25	19	26.0	29.0	25.0	16.0	8.6	9.2	6.7
Range of Measurements	—	—	26.5-30.2	—	—	26-29	28.7-29.15	24.0-25.06	13-16.9	—	—	—

where ε is the electron charge and T is its period of revolution. The magnetic moment m of a current loop is equal to iS

$$m = iS,$$

where S is the area around which the current flows. Clearly,

$$S = T \frac{ds}{dt},$$

and thus

$$m = iS = \varepsilon \frac{ds}{dt}.$$

Comparing this expression with formula (5), we obtain the important relation

$$m = \frac{\varepsilon}{2\mu} \mathbf{j}, \quad (6)$$

from which, using Eq. (4), we have, finally

$$m = n \frac{\varepsilon h}{2\mu \cdot 2\pi}, \quad n = 1, 2, 3, \dots \quad (7)$$

Thus the magnetic moment due to the motion of an electron in an atom must always be an integral multiple of the elementary magnetic moment m_0 , called the Bohr magneton:

$$m = nm_0, \quad m_0 = \frac{\varepsilon h}{2\mu \cdot 2\pi}. \quad (8)$$

Substituting into formula (8) the known values of the universal constants, and converting, as usual, to the magnetic moment per mole, we obtain

$$\text{Bohr magneton} = M_0 = Nm_0 = \frac{N\varepsilon h}{2\mu \cdot 2\pi} = 5584 \text{ G} \cdot \text{cm}. \quad (9)$$

Equations (4), (6), and (7) can be expressed very simply if we measure the angular momentum j and the magnetic moment m of the atom not in cgs units, but in rational units, equal, respectively, to $h/2\pi$ and $\varepsilon h/(2\mu \cdot 2\pi)$, i.e., the Bohr magneton. Then these equations assume the following simple form

$$j = n, \quad n = 1, 2, 3, \dots \quad (4a)$$

$$m = j, \quad (6a)$$

$$m = n, \quad n = 1, 2, 3, \dots \quad (7a)$$

Unless otherwise specified we shall from now on always use this rational system of units.

Let us now turn to the numerical value of the Bohr magneton. As Eq. (9) shows, the Bohr magneton is actually five times (more precisely, 4.98 times) larger than the Weiss magneton, and so, according to the Bohr theory the number of Weiss magnetons in an atom of any substance must always be a multiple of five. This conclusion is definitely in contradiction with experimental data, and the acuteness of this contradiction is in no way related to the

question of the reality of the Weiss magneton. Indeed, Weiss arrived at the concept of the magneton in a purely empirical manner, and the Weiss magneton is *by definition* equal to the largest common divisor of the magnetic moments of the various atoms. Consequently, the magnetic moments of the atoms can in no way be integral multiples of the five times larger Bohr magneton.

How shall we explain this contradiction between theory and experiment? Have we overlooked something in the argument? First, it can be shown that we have taken into account the magnetic field of only the electrons and have forgotten the field of the positive charges, which perhaps also move about in the atom. If we assume, however, that formula (7) also is valid for the positive charges, then the ratio ε/μ for these charges is incomparably smaller than the same ratio for the electrons, and we see that we can neglect the magnetic field of the positive charges with impunity.

A shortcoming of this theory might also be found in the fact that if the magnetic moment of each of the electrons moving in an atom is equal to an integral number of Bohr magnetons, then it is no longer possible to draw any conclusions about the magnetic moment of the atom as a whole: the resultant magnetic moment of the atom is composed *vectorially* of the moments of the constituent electrons, and so depends on the geometric arrangement of the orbits of these electrons. However, from the point of view of the quantum theory this objection is groundless. In order to understand the fundamental importance of the problem we must discuss in detail the so-called space quantization.

3. SPACE QUANTIZATION (RAUMQUANTELUNG)

In general, the quantum theory limits only the *numerical* value of the angular momentum vector j , requiring that this vector assume only integral values.⁵⁾ However, the direction of the vector j remains arbitrary.

If, however, among the possible spatial directions a particular direction is preferred for some physical reason (for example, if it coincides with an electric or magnetic field), then there is an additional constraint on the direction of the vector j : not only must the vector itself assume integral values, but also its *projection* on the preferred (ausgezeichnete) spatial direction must have only integral values.⁶⁾ If we apply this rule to the structure of the atom, as Landé first did,³ then the "preferred" direction must be taken as the direction of the resultant angular momentum (the normal to the invariant plane of the atom). Thus the projection of the angular momentum of each of the electrons on the direction of the resultant must be an integer, and consequently the resultant must also be an integer. In other words, the net magnetic moment of an atom as a whole must be equal to an integral number of Bohr magnetons.

Thus the objection to the quantum theory of magnetons advanced at the end of Sec. 2 is groundless from the point of view of this theory, and the contradiction between theory and experiment remains. This contradiction was for a long time a favorite argument against the Bohr theory

TABLE III.

Number of Bohr Magnetons, n	1	2	3	4	5
Apparent Number of Weiss Magnetons, k	8.7	13.7	18.7	23.7	28.7

until finally in 1920 W. Pauli showed that the contradiction is only rooted in the insufficiently consistent application of the quantum theory.

Indeed, the value of the magnetic moment of paramagnetic atoms and ions is calculated, as we have seen, by the Langenvin formula

$$M = \sqrt{3RC}. \quad (3a)$$

In the derivation of this formula one must determine the average value of $\cos^2 \varphi$, with the assumption that the axes of the atoms can point in any direction in space. However, the theory of space quantization limits the direction of the axes of the atoms to a number of discrete possibilities, and hence the numerical value of $\cos^2 \varphi$ can be substantially changed. According to the classical theory $\cos^2 \varphi$ is always equal to one-third, but according to the quantum theory it depends on the magnitude j of the angular momentum. Since the projection of the vector \mathbf{j} on the preferred direction of the external magnetic field \mathbf{H} must take on only integral values, when $|\mathbf{j}| = n$ (where n is an integer) $\cos \varphi$ can have only one of the following values⁷⁾

$$\cos \varphi = \pm \frac{1}{n}, \pm \frac{2}{n}, \dots, \pm \frac{n-1}{n}, \pm \frac{n}{n}.$$

Therefore

$$\overline{\cos^2 \varphi} = \frac{1}{n} \left[\left(\frac{1}{n} \right)^2 + \left(\frac{2}{n} \right)^2 + \dots + \left(\frac{n-1}{n} \right)^2 + \left(\frac{n}{n} \right)^2 \right].$$

Doing the calculation, we obtain

$$\overline{\cos^2 \varphi} = \frac{1}{3} \frac{(n+1)(2n+1)}{2n^2}.$$

Thus $\overline{\cos^2 \varphi}$ assumes its classical value $1/3$ only in the limit $n \rightarrow \infty$, and in general formula (3a) must be replaced by the following formula (see Eq. (3))

$$M' = \sqrt{\frac{RC}{\overline{\cos^2 \varphi}}} = \sqrt{3RC} \sqrt{\frac{2n^2}{(n+1)(2n+1)}} \quad (3b)$$

$$M' = M \sqrt{\frac{2n^2}{(n+1)(2n+1)}}. \quad (3c)$$

Here M' is the magnetic moment per gram-atom calculated by the quantum theory, M is the same quantity calculated by the classical theory, and n is the number of Bohr magnetons in the atom.

From the quantum point of view, formula (3a), by which the magnetic moment of the atom is usually calculated, is incorrect. It is not surprising that the fictitious values of the magnetic moments obtained with this formula are not integral multiples of the Bohr magneton. On the

other hand, the quantity M' must always be an integral multiple of the Bohr magneton; i.e., the following equality must be valid:

$$M' = n \cdot 5584 \text{ G} \cdot \text{cm}, \text{ where } n \text{ is an integer.}$$

But what must the relation be between the Bohr and the Weiss magneton? The number k of Weiss magnetons in an atom is calculated, of course, from the magnitude of its magnetic moment M , determined according to the classical formula (3a); that is, k is determined from the relation

$$M' = k \cdot 1123.5 \text{ G} \cdot \text{cm}$$

Putting the last two equations into formula (3c) and dividing by (about) 1123.5, we obtain

$$5n = k \sqrt{\frac{2n^2}{(n+1)(2n+1)}},$$

or

$$k = 5n \sqrt{\left(1 + \frac{1}{n}\right) \left(1 + \frac{1}{2n}\right)}. \quad (10)$$

Thus, even though the magnitude of the Bohr magneton is almost exactly five times that of the Weiss magneton, the relation between the number k of Weiss magnetons in an atom (calculated according to classical theory) and the number n of Bohr magnetons in the same atom (calculated according to the quantum theory) is a very complicated one.

It is easiest to understand this dependence with the aid of Table III. The number k of "apparent" Weiss magnetons corresponding to one, two, etc. Bohr magnetons is calculated according to formula (10) and listed in the last row of this table.

This table allows us to check the validity of the theory.

Actually, if the quantum theory is correct, then an analysis of the experimental data according to the classical formula (3a) must necessarily give one of the following values of k for the number of Weiss magnetons (in round numbers): 9, 14, 19, 24, etc.

Pauli believed that this test could be carried out only for paramagnetic *gases*: in solids and liquids the internal molecular forces are too strong to speak of space quantization relative to an external magnetic field.

Only two paramagnetic gases are known: NO and O₂. The apparent number of Weiss magnetons k according to the most recent measurements vary from 8.9 to 9.2 for NO and from 13.9 to 14.12 for O₂. The agreement of these numbers with the numbers in the last table ($k=8.7$ and $k=13.7$) is quite satisfactory; we can infer that NO has *one* and O₂ has *two* Bohr magnetons. That is, each oxygen atom has one Bohr magneton.

Although this quantitative agreement comes down strongly in favor of the quantum theory, it must be pointed out that the Pauli theory presented refers only to monoatomic gases, and for the case of the diatomic gases NO and O₂ one would have to take into account the thermal rotation of the molecule. It would appear very probable *a priori* that the rotation smears out the influence of the space quantization. However, the agreement between the elementary theory and experiment shows that the thermal rotation does not disrupt the discrete quantized orientation of the magnetic axes. This fact can only be explained if we make the unlikely assumption that the magnetic axes of the NO and the O₂ molecules are perpendicular to their axes of symmetry (i.e., the lines joining the centers of the atoms).

In any case, whatever difficulties there may be in the further development of the theory, one thing is certain: by pointing out the incorrectness of the Langenvin formula from the point of view of the quantum theory, Pauli proved groundless the objections to the quantum theory of magnetism based on the apparent contradiction between this theory and the "direct" measurements of the atomic magnetic moments.

A few reported works of Pauli (1920) contain essentially all the basic tenets of the present-day theory of atomic magnetism. Further development of the theory has consisted of working out the details and an experimental verification of these tenets.

4. DIRECT DEMONSTRATION OF SPACE QUANTIZATION

We have shown that the principal premise of the quantum theory of magnetism is that the orientation of the atoms has a discrete quantized nature. It is natural, therefore, that a direct experimental demonstration that the orientation is quantized should be of enormous significance for the entire theory. The way to achieve such a demonstration was pointed out by O. Stern in 1921, and the actual experimental was performed by him in collaboration with W. Gerlach in 1922.

This experiment is remarkable in its simplicity, and is probably the most direct of all known experimental verifications of the quantum theory. The persuasive power of this experiment is so great that, influenced mainly by the success of this experiment, M. Planck in the fifth edition (1923) of his famous book, *Theorie der Wärmestrahlung*, abandoned his second version of the quantum theory of radiation.⁸⁾

In view of the wide reknown that the Stern–Gerlach experiment has enjoyed,⁹⁾ I may confine the discussion to only the most important aspects. The problem that Stern faced was to measure the magnetic moment of the atom, or, more precisely, the component of this moment in the direction of an external magnetic field. Stern pointed out that for this purpose it is sufficient to measure the mechanical action of the field on the atom *under the condition that the field is nonuniform*. In a nonuniform magnetic field, in addition to couple forces, which tend to rotate the atom and align its axis in the direction of the field, the atom also sees a net force on its center of mass. Let us assume for

simplicity that the direction of the gradient $\partial H/\partial s$ coincides with the direction of the field H . Then, clearly, the atom will be acted on by a resultant force

$$F = m \frac{\partial H}{\partial s} \cos(m, H),$$

where the magnetic moment m must, of course, be expressed in cgs units, and not in rational units.

In this way, the magnitude F of this force depends on the projection m in the direction of the field H , that is, on the quantity $m \cos(m, H)$. By measuring the force F and the gradient $\partial H/\partial s$ it is thus possible to measure $m \cos(m, H)$.

According to the classical theory, any value of $\cos(m, H)$ from 0 to 1 is possible, whereas according to the quantum theory all the atoms are divided into several distinct groups, each group corresponding to one specific value of the projection $m \cos(m, H)$. Observations of the deflection of atoms in a nonuniform magnetic field by the force F should provide a decision as to which of these theories is correct.

In practice, this *experimentum crucis* was carried out in the following way. The element silver was evaporated in a high vacuum,¹⁰⁾ and two diaphragms with apertures of dimensions 0.5×0.05 mm separated out a narrow beam of atoms from the atomic flux emanating from the surface of the molten silver. This atomic beam was passed along the wedge-shaped pole of an electromagnet at a distance of several tenths of a millimeter from it and then was caught by a cooled glass plate. Near the pole the magnetic field gradient $\partial H/\partial s$ reached 150 000 G/cm, with the direction of the gradient in the same direction as the direction of the field. Figure 1 shows a photomicrograph of the silver deposit, magnified 40 times, obtained from the glass plate with the magnetic field turned off, while Fig. 2 shows the deposit (the trace of the beam) obtained with the magnetic field on. In the latter case the silver beam is distinctly split in two, with some of the atoms attracted toward the magnet pole and some repelled from it.

It is thus seen that the atoms are divided into two and only two groups, with the axes of the atoms of one group pointing along the field and the axes of the atoms of the other group pointing against the field. The intermediate case is completely absent.

This experiment thus demonstrates, first, the fact of quantization of the orientation in a magnetic field, and, second, the presence of one magneton in the silver atom. The latter result is clear by virtue of the fact that, as shown on p. 19 the number of possible orientations of the axis of the atom is twice the number of magnetons in the atom.

Moreover, the Stern–Gerlach experiment makes it possible to measure the magnitude of the magnetic moment of silver, that is, the value of the Bohr magneton. To do so, one need only measure the deflection of the beam in the magnetic field and the gradient $\partial H/\partial s$, and also the time that an atom is subjected to the action of the deflecting force. The latter is determined from the length of the path in the magnetic field and the velocity of flight (this velocity was measured directly by Stern in 1920 under the same

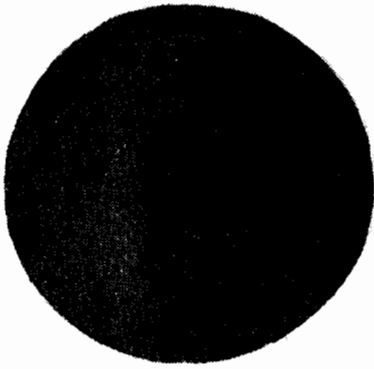


FIG. 1.

experimental conditions). The average value of the magnetic moment of the silver atom, as inferred from two different experiments, is equal to

$$mN = M = 5475 \pm 5\% \text{ G} \cdot \text{cm}$$

per gram-atom, which is in excellent agreement with the theoretical value of the Bohr magneton of $M_0 = 5584 \text{ G} \cdot \text{cm}$.

Thus the experiments of Stern and Gerlach provide a brilliant confirmation of the quantum theory of the magneton.

Two questions naturally arise in connection with the success of this experiment. How does the axis of the atom come to be aligned in a quantum-permitted direction? and what happens when the direction of the external field is changed? Does the axis of the atom follow continuously the direction of the field? In an exceedingly interesting joint paper, Einstein and Ehrenfest examined a number of possibilities and arrived at the following rather discouraging conclusions.

Every change in the orientation of the axis of an atom in an external magnetic field must be accompanied by the emission or the absorption of the corresponding amount of energy. If this emission or absorption of energy were to occur according to classical laws, then the quantum-related alignment of the axis of the atom would require a time 10^{14}

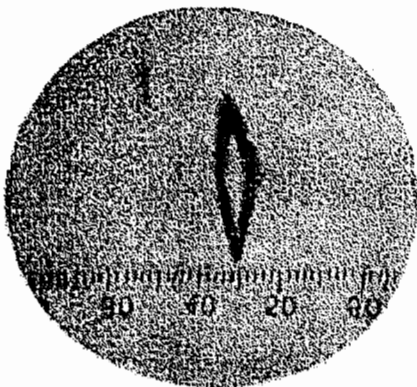


FIG. 2.

times longer than the flight time of an atom in the Stern-Gerlach experiment. We could abandon the classical view and conclude that when the direction of the field changes the direction of the axis of the atom at first lags behind the field and then aligns itself abruptly, while the energy is emitted (or absorbed) in accordance with the quantum laws. However, this idea would require that we make a completely irrational distinction between systems that can radiate (charged systems) and systems that cannot radiate (uncharged systems). To introduce such a distinction runs contrary to our notions regarding the specific heat of solids and gases.

Finally, if we assume that the axis of the atom tracks instantaneously each change in the direction of the field, then we come up against contradictions with the laws of mechanics.

Thus the great successes of the quantum theory entails a number of perplexing and unresolved questions.

5. THE BOHR AND WEISS MAGNETON

Despite the mentioned difficulties in its theoretical interpretation, the Stern-Gerlach experiment has strongly reinforced the theory of Pauli, which we advanced in Section 3. Among the shortcomings of this theory must be included the extremely limited range of direct application of the theory (two paramagnetic gases). Pauli decided not to apply his formulas to liquids and solids, assuming that the interatomic forces in these materials, the hydration of the ions in solution, etc., would change the nature of the orientation of the elementary magnets beyond recognition. These arguments seemed so obvious and irrefutable that Sommerfeld in 1923 (Ref. 12), discussing the report of Cabrera (see Sec. 1) and calling attention to the theory of Pauli, regarded it necessary to emphasize the inapplicability of this theory to solids and liquids. Meanwhile, one needs only to compare the summary of the experimental data (Table II) with the theoretical data (Table III) to be persuaded of the undeniable applicability of the quantum theory to paramagnetic matter of any state of aggregation.¹¹⁾

According to the quantum theory of magnetism, one, two, ... real Bohr magnetons must correspond (in round numbers) to 9, 14, 19, 24, 29, ... apparent Weiss magnetons. However, for the ions of the iron group the following values of k of Weiss magnetons have been determined by experiment (also in round numbers): 9 has been found twice, 19 twice, $k=24$ has been found once, and the close number 25 has been found twice, and finally $k=29$ has been found twice. All these seven values are in complete agreement with theoretical predictions. The remaining three values are

$$k = 6.7 (V''''), \quad k = 16 (\text{Ni}''), \quad \text{and} \quad k = 26 (\text{Fe}'').$$

Data for Fe are the least reliable: various determinations fall between 26 and 29. Finally, the data for V^{IV} have been taken from old and relatively inaccurate measurements of Pascal.¹²⁾ This coincidence between the results of measurements and theoretical predictions is also found for other paramagnetic substances, as is clearly seen in Table IV, in which only ferromagnetic metals,¹³⁾ complex compounds, and the rare earth elements are left out. The second column lists the theoretical values of the number k corresponding to one, two, ... Bohr magnetons. The next column lists those values rounded off, and finally the fourth column lists the experimentally determined values of k for the various substances. These values differ appreciably from the theoretical values in only three instances.

While bearing in mind the low accuracy of most of the experiments, one cannot but admit that the agreement between theory and experiment is better than satisfactory. This agreement is all the more surprising and unexpected in that we did not take into account intermolecular interactions, which, of course, cannot help but distort the results of the quantization of the orientation in the external field.

In order to account for the unexpected success of this undeniably incomplete theory we need only appeal to the fact that all the magnetometric measurements have been carried out in very strong fields. It is clear that for space quantization the decisive factor is the ratio between the force of this field and the force of the molecular fields.

In this connection it is interesting to recall that in many crystals, even in relatively weak fields, a marked Zeeman splitting is observed in the absorption spectrum and in the fluorescence spectrum, which no doubt shows that the external field dominates the internal fields. In any case, it cannot be entirely accidental that all the measured values of the number k are definitely grouped around five definite, theoretically *predictable* numbers. It should also be noted that the quantum theory attributes to the measured atoms a small number of magnetons (up to 5), whereas according to Weiss, many atoms have over 20–25. Obviously such a large number k considerably reduces the credibility of the Weiss theory: in the long run, with such large integers one can come as close as one wants to any sequence of any numbers.

Finally, it is necessary to take into account that the quantum theory provides an *a priori* calculation of the magnitude of the magneton without the aid of any experimental data and with the use only of the universal constants (ε , μ , and h).

It only remains to be stated one more time that the simplest and seemingly least probable assumptions (the applicability of quantization to matter of any state of aggregation) are far from being always wrong.

The persuasiveness of the quantum theory is enhanced when one examines the dependence of the magnetic moment of ions on the number of outer (valence) electrons. We shall, however, postpone the discussion of this issue until we introduce one more completely independent means of determining the number of magnetons in an atom, that is, the spectroscopic method.

6. SPECTROSCOPIC METHOD OF DETERMINING THE MAGNETIC MOMENT OF AN ATOM

The topic of atomic magnetism has been of decisive importance in the past few years in the further development of the theory of spectra. Occupying the central point of this theory are two questions that the elementary quantum theory is powerless to answer. These have to do with the nature of the multiplicity (Multiplizität) of most spectral lines (doublets, triplets, etc) and the anomalous nature of the splitting of these lines in a magnetic field (the anomalous Zeeman effect).¹⁵⁾ We now know that the inability of the theory to address these questions is explained by the fact that they are directly related to the magnetic properties of the atoms.

At the present time we can regard it as established that all magnetic properties of atoms are anomalous.¹⁶⁾ The reason for this is clearly that the ordinary laws of electromagnetism are inapplicable even to the stationary states of the atom. The need to modify the fundamental laws of mechanics and electrodynamics has definitely been established by all the modern developments in the quantum theory, but the inadequacy of the classical viewpoint is perhaps nowhere so clearly evident as in the study of magnetism (Landé, Ref. 18).

It is understandable, therefore, that for a time all attempts to understand the internal "magnetic" mechanism of atoms ended unsuccessfully; then in the last few years, thanks mainly to the work of Landé, Sommerfeld, and Heisenberg, it was found possible to construct a purely formal theory, or rather, a systematic numerical scheme that encompasses in a unified way all these complex phenomena. This theory has so far been found to be in excellent agreement with experiment, and a whole series of its predictions have already been verified experimentally. Only because of this theory has it been possible finally to decipher such complex spectra as, for example, those of Mn, Cr, Fe, and others. However, this theory is still in the development stage, and moreover, because of its formal nature, it admits of a number of different interpretations. Even yet, the statement of the theory by different investigators differs not only in essence, but even in the choice of the basic quantities and their meaning. I do not plan to discuss this theory in detail, but shall only give a brief account of it, since it leads to a new spectroscopic means of determining the magnetic moment of atoms. We shall restrict the discussion to the form of the theory used by Sommerfeld, first, because this theory is somewhat simpler than the theory of Landé, and, second, because Sommerfeld has applied his theory to the question of the magneton¹⁷⁾ (see Ref. 15).

The multiplicity of the spectral lines obviously stems from the multiplicity of the stationary states of the atom. Generally speaking, the difference in the states of the atom lies in the difference in the orbit of the outer electron (Leuchtelektron), and the nature of this orbit also determines primarily the internal energy of the atom. Each orbit is characterized by two quantum numbers: the so-called principal quantum number (Hauptquantenzahl) and the azimuthal quantum number (n and k in the notation of

Bohr). However, only in the very simplest cases (H and He⁺) are these two numbers sufficient for an exhaustive determination of the state of the atom. In general the same pair of quantum numbers n and k can correspond to several more or less close-lying energy levels. The existence of these finer subdivisions of the energy levels is also observed in the multiple structure of the spectral lines.

The cause of the splitting lies in the possibility of different orientations of the orbit of the outer electron (or electrons) relative to the "core" of the atom (Atomrumpf; the so-called combination of the nucleus and the inner electrons). It is believed that the core of the atom constitutes a more or less bound entity and that the axis of the core can take on various orientations relative to the plane of the orbit of the outer electron, while at the same time obeying the laws of quantization. To the different orientations of the core correspond different potential energies of the core in the magnetic field of the outer electron. Thus in order to characterize fully the state of the atom it is necessary to specify the angle between the plane of this orbit the axis of the core in addition to the quantum numbers n and k that determine the orbit of the outer electron. For this purpose it is sufficient to specify the resultant angular momentum of the atom, which is the geometrical sum of the angular momentum of the outer electron and that of the core of the atom and thus depends on the orientation of the axis of the core. The number that expresses the magnitude of this net angular momentum in rational units ($\hbar = h/2\pi$) is called the *internal quantum number* and is denoted by the letter j . Unlike the usual quantum numbers, it can assume not only integral, but half-integral values (multiples of one-half). In this way, the same value n_k can correspond to several different internal quantum numbers, and thus to several energy levels of the atom. For example: the yellow doublet D₁ and D₂ of sodium correspond to the initial orbits 2p₁ and 2p₂, the former of which is characterized by the quantum numbers, $n=2$, $k=2$, and $j=1/2$, while the latter corresponds to the quantum numbers $n=2$, $k=2$, and $j=3/2$.¹⁸⁾

Let us now turn to the Zeeman effect. In the absence of an external field the direction of the atomic axis, that is, the direction of its resultant angular momentum j , is completely arbitrary. When an external magnetic field is applied the laws of space quantization come into play, and the direction of the atomic axis is limited to a number of discrete possibilities. The orientation of the atom is characterized by the angle between the direction of the field H and the direction of the angular momentum vector j . The

quantization rule reduces to the statement that the projection j_H of the vector j on the direction of H ($j_H = j \cos(j, H)$) must be either $\pm j$ or different from that by an integral number of units. For example, for $j=3/2$ there are four possible values of the projection j_H :

$$\pm 3/2 \quad \text{and} \quad \pm 1/2.$$

Depending on the orientation of the atom, its potential energy also varies in an external magnetic field. This energy is

$$\Delta E = -mH \cos(m, H), \quad (11)$$

where m is the magnetic moment of the atom, expressed this time not in rational units, but in ordinary cgs units.

Thus the same set of values of n , k , and j can correspond to a number of different energies of the atom (depending on $\cos(m, H)$). In other words, in a magnetic field each spectral term (energy level) is split into a number of close-lying terms corresponding to the different orientations of the magnetic axis of the atom. This also explains the magnetic splitting of the spectral lines (the Zeeman effect).

The magnitude of the splitting ΔE of the terms can be measured spectroscopically. On the other hand, the direction of the vector m , of course, coincides with the direction of the vector j , i.e.,

$$\cos(m, H) = \cos(j, H).$$

Thus in Eq. (11) the values of ΔE and H can be measured directly, while the value of $\cos(j, H)$ is determined by the quantization rules, and so this equation makes it possible to use measurements of the Zeeman effect to calculate the atomic magnetic moment m .

It can be shown that we have complicated a simple problem to no purpose. We have already alluded many times to the well known relation between the angular momentum and the magnetic moment

$$m = \frac{e}{2\mu} j \text{ (Eq. (4)).}$$

We have pointed out that if m and j are measured in rational units (equal, respectively, to $h/2\pi$ and to the Bohr magneton $e\hbar/(2\mu \cdot 2\pi)$), then Eq. (4) reduces to the numerical equality of the numerical values of the angular momentum and the magnetic moment of the atom

$$m = j. \quad (4a)$$

The quantity j in this formula is none other than the internal quantum number; i.e., the number of magnetons m in an atom must be simply equal to the internal quantum number j .

Thus it can be shown that to determine the magnetic moment m there is no need to measure the Zeeman effect.

Unfortunately, however, the matter actually is much more complicated, as is shown mainly by the anomalies in the Zeeman effect observed most spectral lines. The elementary theory, which is based on the equality (4a) requires that all lines have the normal Zeeman triplet. To explain the experimental data one must assume that the

TABLE IV.

n	k	
1	8.7	9 Ag ($n=1$), Cu $''k=9-10$, V $''9.2$, V $''''9$, Ti $''8.6$, NO 9.2, Pt 8-9, Pd ~ 8
2	13.7	14 O $_2$ 14, V $''''14$, Ni $''16(?)$
3	18.7	19 Cr $''19$, Mn $''''19$
4	23.7	24 Co $''24$, Cr $''24$, Mn $''25$, Fe $''26(?)$
5	28.7	29 Fe $''29$, Mn $''29$

relation between the magnetic moment and the angular momentum is much more complicated than is assumed by the classical theory, and that equality (4a) should be replaced by the relation

$$m = gj. \quad (12)$$

Introducing the factor g into this formula brings in the so-called "splitting factor" (Aufspaltungsfaktor), which is a very complicated function of the azimuthal quantum number k , the internal quantum number j , and, finally, a third number r , which characterizes the so-called maximum multiplicity of the terms of the given spectral series.¹⁹⁾

To determine m it is therefore insufficient to know only j , and one must have recourse to the method outlined above, which is based on the measurement of the splitting ΔE of the terms. This method, as already mentioned, permits a direct determination of m ; then by means of formula (12) one can also calculate $g = m/j$.

It should be acknowledged that by replacing the equality $m = j$ (Eq. (4a)) by the relation $m = gj$, the quantum theory of magnetism, strictly speaking, cuts the ground from under our feet, for equality (4a) is based on the fundamental laws of electromagnetism, the very foundation of the concept of the Bohr magneton.

Here we must again make reference to a most characteristic feature associated with the development of modern physics—the accumulation of deep internal contradictions in new fruitful theories. Nonetheless, it is these contradictions that in many cases point us towards the discovery of new laws—laws that are so simple and persuasive that they undoubtedly correspond to the true nature of matter.

This is the situation in the case we are studying. The factor g was introduced by Landé¹¹ only in order to explain the anomalous Zeeman effect in the twofold and threefold spectral lines (doublets and triplets). A natural generalization of this theory then allowed him to predict the complex structure of multiple lines (multiplets) and the nature of their splitting in a magnetic field. These theoretical predictions made it possible to work out for the first time the extremely complicated and tangled field of spectral analysis and they were brilliantly confirmed by experiment. At present scarcely a month passes that does not see new successes in this area.²⁰⁾ If only for this reason the merit of the theory is very great. However, it turns out that the same theory is able, almost without any additional assumptions, to "explain" the anomalous magneto-mechanical effect.²¹⁾

Finally (for our purposes this is of the highest importance), one can on the basis of this theory determine the number of magnetons in an atom, with the results in full agreement with the results of direct magnetic measurements.

As already mentioned, to determine the magnetic moment of an atom it one must use formula (12). We shall not go into how one determines the values of g and j corresponding to a specific state of an atom, since this would take us too far afield. We only recall a simple rule

that in a number of cases gives a direct determination of the value of m .

Of all the quantum numbers that characterize the state of the atom, the most important is the azimuthal quantum number k . Later we shall refer to single-quantum, two-quantum, and so forth, states, meaning thereby the value of the quantum number k , since the principal quantum number n has no bearing on the angular momentum or the magnetic moment of the atom. We recall again that in spectroscopic notation the letters s, p, d, \dots are used to designate the orbits corresponding to $k=1, k=2, k=3, \dots$

Having decided on the terminology, we can formulate in the following way the Sommerfeld rule: In the normal single-quantum state s ($k=1$) the number of magnetons in an atom is one less than the maximum multiplicity of its energy levels.²²⁾ For example, for an atom such as Ca that emits simple lines the maximum multiplicity of the lines is 1; so that the number of magnetons is $m=1-1=0$. For atoms that emit doublets (e.g., Na) the maximum multiplicity is 2, and consequently $m=2-1=1$; for atoms that emit triplets (e.g., Ca) the maximum multiplicity is 3, and consequently

$$m = 3 - 1 = 2, \text{ etc.}$$

Calcium atoms can emit single lines as well as triplets, and thus these atoms can be in two different states. To distinguish these states they are customarily denoted in spectroscopic notation by capital and lower-case letters, S, P, D, \dots , and s, p, d, \dots . In the S state (simple lines) the number of magnetons is zero, and in the s state (triplet) the number of magnetons is two. Of course, this simple rule is applicable only to the normal single-quantum states of the atom. In an excited state of the atom its angular momentum j is changed, and so the magnetic moment m is also changed.

It is necessary, finally, to note that some materials, even under ordinary conditions, are found in multiple-quantum states ($k > 1$), which for these materials are thus normal. Such a situation is found, for example, in the vapors of Al and Tl (normally $2p$) and Fe vapor (normally $3d$), and so forth. The simple Sommerfeld rule does not apply to these materials.

7. MAGNETISM AND THE PERIODIC TABLE

One of the best confirmations of the quantum theory of magnetism is the complete agreement between the results obtained by totally different methods (spectroscopy and direct magnetic measurements). Figure 3 shows a diagram due to Sommerfeld, which displays the results of measurements of the group of elements whose magnetic properties have been most thoroughly studied. The number of "outer" electrons²³⁾ is plotted along the horizontal axis, and the number of magnetons along the vertical axis. Above the number of outer electrons stands the total number of electrons in the atom and the name of the corresponding neutral atom. The results of spectroscopic measurements are indicated by the underline below the element symbol; the rest of the values were taken from the usual magnetic methods of measurement (see the summary in

Table IV). The number of magnetons is rounded off to whole numbers; this can induce doubt only for the case of Ni'' and Fe'' .²⁴⁾

The diagram is augmented by some data not included by Sommerfeld (data for K, V'' , V'''' , Mn'''' , Fe'' , and Cr). I calculated the number of magnetons for Fe on the basis of new spectroscopic work of Hilda Gieseler and W. Grotrian (Ref. 16).²⁵⁾ Two values are given for some atoms (Ca, Cr, Mn), since these atoms can exist in two different single-quantum states S , and this circumstance shows up in the presence of two different systems of spectral lines. For example, the Ca atom can emit both simple lines and triplets, and Cr can emit quintets and sextets, and so forth.

Immediately upon inspection the diagram is seen to exhibit a strict regularity, which is evidence for the complete agreement between the results obtained by the two entirely independent methods (magnetic measurements and spectroscopy).

Particularly conspicuous is the straight line that passes through the origin at an angle of 45° . The entire line is occupied by points that are in mutual agreement. The magnetic moments of all 15 atoms and ions lying on this line conform to the following simple and convincing rule: The number of magnetons in an atom is equal to the number of outer (valence) electrons. When the atom loses electrons by ionization it also loses magnetons. For example: Mn has 7 electrons and 7 magnetons ($m=7$), while for Mn'' $m=5$, and for Mn''' $m=4$, and finally, for Mn'''' $m=3$. The rule is confirmed in a particularly convincing way by the agreement of the number of magnetons for ions of completely different kind but with the same number of outer electrons. An example is $m=1$ for K, Ca' , Ti''' and V'''' .

Let us now turn our attention to the straight line lying somewhat below the former one, where a large number of points are situated.²⁶⁾ The numbers of magnetons at the corresponding points of these two lines differ exactly by two. For example: for Ca, $m=2$ and $m=0$; for Cr, $m=6$ and $m=4$, and for Mn $m=7$ and $m=5$.

Without attempting to examine in detail the internal mechanism, we can interpret this result in the following way. The maximum number of magnetons in an atom is equal to the number of outer electrons and corresponds to the revolution of all these electrons in the same direction. However, if one of the electrons happens to revolve in the retrograde direction, then its magnetic field will neutralize the field of one of the direct-revolving electrons, and the resulting magnetic moment of the atom is reduced by two. For example: Ca has two valence electrons; when both of them revolve in the same sense, then $m=2$, and if they revolve in the opposite sense, then $m=0$. Another example is Fe'' : it has six electrons and $m=4$, so that one of the electrons revolves in the opposite direction. This retrograde electron obviously is less tightly bound to the atom and therefore is the first one removed with subsequent ionization. Therefore the ionization of Fe'' results not in a decrease, but in an increase in the resultant magnetic moment of the atom: for Fe''' , $m=5$ (all five remaining electrons revolve in the same direction).

Obviously, an atom may have not only one, but several retrograde electrons. For example, for Ni'' the total number of outer electrons is 8, and $m=2$; hence one must conclude that it has three "retrograde" electrons that neutralize three "direct" electrons.

At any rate, in whatever way we regard these attempts to obtain an intuitive interpretation, the diagram shows beyond doubt that the following rule holds: The number of magnetons in an atom can be either equal to the number of outer electrons or less than that by an even number (mutually cancelling electrons drop out pairwise). The consequence is that in atoms with an even (odd) number of electrons the number of magnetons is always even (odd).

The only exception to this rule is the Co'' ion, which has 25 electrons and 4 magnetons. It should also be noted that the magnetic moment of the Ni'' ion may be equated to two magnetons only by stretching things somewhat (see Table IV).

Save for these exceptions, this rule has been confirmed not only for the elements of the iron group, but also for all the generally known materials related to magnetism and monatomic gases. We cite, for example, the diamagnetism of the inert gases, the results of the Stern-Gerlach experiment with silver, and the spectroscopic laws of displacement and replacement²⁷⁾ (Erschiebungssatz and Wechsel-satz), and so forth.

Strong paramagnetism is found only in certain regions of the Periodic Table (the eighth-group triad and the rare earth elements); that is, only where the number of magnetons is a maximum, equal to the number of outer electrons in the atom. This is probably related to the fact that these are the regions of the Periodic Table where new electrons are added to the inner layers of the atom. However, generally speaking the inner state of the atom are set up according to the minimum possible value of the magnetic moment (one magneton for the odd columns of the Periodic Table and zero magnetons for the even columns).

Thus if we set aside the question of Co'' , then all the rest of the experimental data fit into the orderly scheme of Sommerfeld, striking and attractive in its extreme simplicity.

Nevertheless, just because of its simplicity, this scheme is utterly incomprehensible.

The fact is, the rule of Sommerfeld regarding the number of magnetons in an atom appears so convincing because it is automatically connected with the idea of the extremely simple intraatomic mechanism. This rule clearly must be understood in the sense that in the normal state of the atom all of its outer electrons move in single-quantum orbits (single-quantum in the sense of the azimuthal quantum number of the orbit n_1), so that each electron corresponds to one magneton. Moreover, the orbits of all the electrons are arranged in a common plane, so that the geometric summation of the magnetic moments of the individual electrons is replaced by an arithmetical summation. *However, not one of these assumptions can hold up against even the smallest criticism* from the point of view of our present-day understanding of the structure of the atom. On the contrary, the extreme complexity of the or-

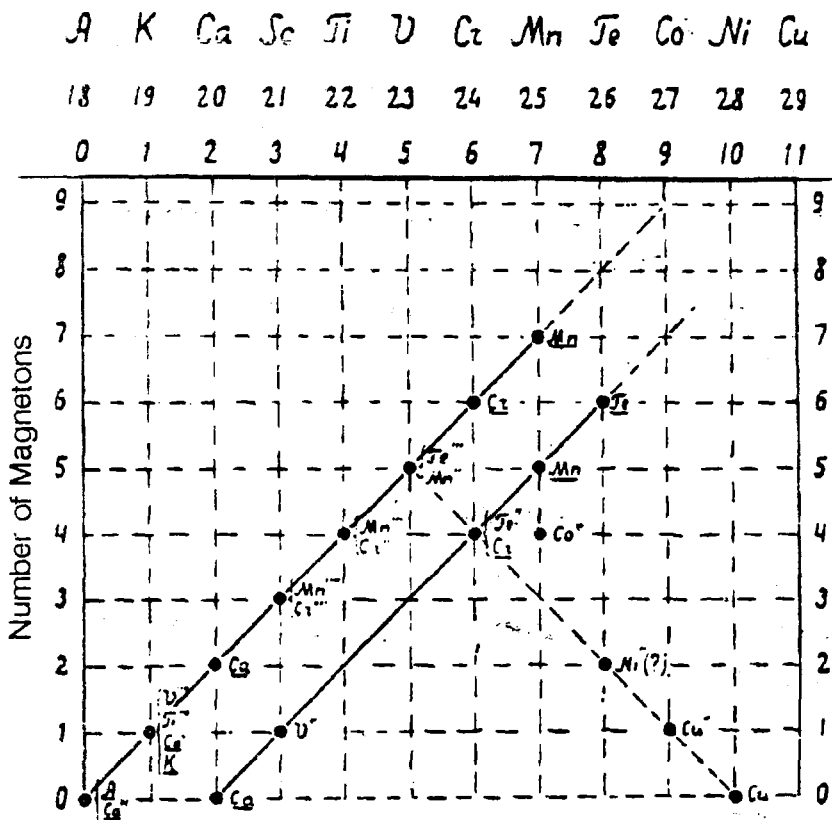


FIG. 3.

bits of the valence electrons can be taken as solidly established; the planes of these orbits in any case are not parallel, and finally some of the valence electrons definitely do not move in single-quantum orbits.

Nonetheless, one cannot regard Sommerfeld's rule of the number of magnetons in an atom as a purely mnemonic device without any physical substance. The extreme simplicity and intuitiveness of Sommerfeld's scheme and its complete verification by experiment is a clear indication that this scheme expresses some new important law of atomic structure. We cannot understand this quantum rule, discrete by its very nature, because in its present condition the quantum theory rests on an internally inconsistent base. Research into laws similar to those of Sommerfeld must also create the possibility of placing a new and solid foundation beneath the quantum theory.

8. DIFFICULTIES OF THE QUANTUM THEORY OF MAGNETISM

The present-day quantum theory bears the imprint of internal inconsistencies; all of its successes have generated new difficulties for it. Such has been the fate of the theory of magnetism. We have already had occasion to mention the theoretical difficulties that have arisen in connection with the success of the Stern-Gerlach experiment. Let us now turn to difficulties of another type.

So far we have avoided by silence the following fact. According to the presently accepted model of helium (the "crossed" model of Landé) the helium atom must have a magnetic moment, and consequently paramagnetic proper-

ties. Nonetheless, helium is strongly diamagnetic. How can we escape from this contradiction? There are two ways. First we can assume that in contradiction to all the known laws of electrodynamics the helium atom has no magnetic moment: Bohr, for example, has expressed the notion of electron orbits that are "dead" with respect to magnetism (magnetischtot). This is what the formal theory of Sommerfeld reduces to in essence, assigning to helium an internal quantum number j equal to zero (the angular momentum equal to zero).

On the other hand, while not denying the existence of a magnetic moment in the helium atom, one can take the view that in a magnetic field the axis of the helium atom is aligned *perpendicular* to the field rather than along it (this assumption, of course, also contradicts the laws of quantum mechanics). Landé takes this point of view, and we shall now give a brief exposition of this theory (Ref. 11).

In Sec. 6 we stated that from the spectroscopically measured magnetic splitting of the energy levels of the atom

$$\Delta E = -mH \cos(m, H) \quad (11)$$

one can determine the magnetic moment m of the atom. However the solution of this equation is not unique. By direct experiment one can obtain only

$$m \cos(m, H) = -\frac{\Delta E}{H},$$

but the way in which the product $m \cos(m, H)$ is decomposed into its factors is arbitrary, and one can determine

the value of m only by applying the space quantization rule. This is how the formulation of these rules of the Landé theory differs from the theory of Sommerfeld. Without going into detail we only mention some of the final conclusions of the Landé theory.

According to the Landé theory, space quantization of the orientation along the axis of the field is forbidden, so that the axis of the atom is always inclined to the direction of the field. For the helium atom (for which the internal quantum number is $j=1/2$ according to Landé) only a single unique arrangement is possible, namely, the perpendicular one, which is thus in full agreement with the diamagnetism of the helium atom.²⁸⁾ The Stern-Gerlach experiment is explained by Landé in the following way: the silver atom has not one, but two magnetons ($j=1, g=2, m=gj=2$), and in a magnetic field the axis of the atom is aligned at an angle of 60° , so that $\cos \varphi = \pm 1/2$. Consequently, the projection of the magnetic moment on the direction of the field is equal to

$$m \cos \varphi = 2 \times (\pm \frac{1}{2}) = \pm 1,$$

which agrees entirely with the results of the Stern-Gerlach experiment. It is curious therefore that in the opinion of one of the leading experts in this field, even this extremely simple experiment is deficient in that it has a very complex and unconvincing interpretation. If we consider in the context of the Landé theory what the number k of "apparent" Weiss magnetons is that corresponds to one, two, etc. Bohr magnetons, we obtain the same values 8.7, 13.7, ..., as in the Pauli-Sommerfeld theory (Table V). As we have seen, this prediction of the two theories is well supported by experiment. The only difference between the theories in this context cannot be resolved by experiment; the difference lies in the nature of the correspondence between the numbers k and n and is readily illustrated in Table V.

In general, it must be said that despite the difference in the interpretation of the experimental facts, *all* of these facts are equally well explained by either theory. An *experimentum crucis* to decide between them is not possible because these theories as yet are essentially only productive formal schemes for systematization of experimental data.

By comparison with the Landé theory, the initial Pauli-Sommerfeld theory was distinguished by a greater simplicity, but later it was found necessary to introduce into this theory some complicating corrections.

Indeed, in Sec. 3, in the derivation of formula (3b) and in the calculation of Table III, we used as a basis the equality (in rational units)

$$m = j. \quad (6a)$$

Then in Sec. 6 we found it necessary to introduce the splitting factor g :

$$m = gj. \quad (12)$$

This complication entails the necessity of a corresponding change in formula (3b), since space quantization applies to the vector \mathbf{j} and not to the vector \mathbf{m} . Let us illustrate this by an example.

Let us take $m=3$; then according to the initial theory of Pauli we also have $j=3$, and there are six different orientations available to the axis of the atom, corresponding to

$$\cos \varphi = \pm 1, \pm \frac{2}{3}, \pm \frac{1}{3}.$$

therefore

$$\overline{\cos^2 \varphi} = \frac{14}{27} = 0.52.$$

When the corrected formula is used it is necessary to make a specific assumption about g . If the atom is in the normal S state, then, as we already know, $g=2$, and therefore $j=3/2$ for $m=3$. Consequently four different orientations are possible for the atom, corresponding to

$$j_H = j \cos \varphi = \pm \frac{3}{2}, \pm \frac{1}{2}, \text{ i.e., } \cos \varphi = \pm 1, \pm \frac{1}{3},$$

since, according to the quantization rule, the projection j_H must be either equal to j or differ from it by an integer.²⁹⁾ Consequently

$$\overline{\cos^2 \varphi} = \frac{5}{g} = 0.56.$$

Thus the results of the corrected and of the initial theory are very close. A more complete comparison of the two theories is given in Table VI.

Comparing the numbers in Table VI with the experimental data listed in Table IV, we can readily note that the agreement of the theory with experiment is not only not destroyed by the corrections, but perhaps is even improved.

At the present time the introduction of this correction to the initial theory is regarded as necessary by Sommerfeld as well as by Pauli himself.

Thus the success of the initial theory is accounted for only by a more or less fortuitous circumstance: the effect of the correction factor g on the final results of the calculations is small.

In summary, the quantum theory of magnetism has experienced the fate of all quantum theories (and non-quantum theories as well): The initially simple concept has been extraordinarily complicated and encumbered by an abundance of details and corrections. However, incomparably more serious is the fact that this theory is torn by *internal* contradictions. Indeed, all of quantum theory, the calculation of the stationary orbits, even the calculation of the Bohr magneton, rests on the application of classical electrodynamics to the stationary states of the atom. By abandoning the relation

$$m = j,$$

and introducing the completely incomprehensible, classically unfounded splitting factor g , we thereby remove all the theoretical foundations of the theory. Lack of space, unfortunately, does not allow us to dwell on even more serious paradoxes, by comparison with which even the "anomaly" in the splitting factor g is only an insignificant violation of the laws of mechanics³⁰⁾ (Landé, Ref. 17).

TABLE V.

True Number n of Bohr Magnetons	0	1	2	3	4
Apparent Number k of Weiss Magnetons	0	8.7	13.7	18.7	23.7
Apparent number k of Weiss Magnetons According to Lande	0	0	8.7	13.7	18.7

But how shall we relate to this complicated and internally contradictory theory? A half century ago such a theory could not have been acknowledged or responded to. Much has changed since that time. Then there prevailed the self-assured confidence that the fundamental shape of the physical picture of the universe was known, and it remained only to fill in the details. It is natural that then the main criterion for the suitability of a new theory was its logical coherence and simplicity. Now, we have seen that the laws that direct the elementary internal processes are totally unknown. The complication and the inconsistency of present-day theory—let us recall the Bohr correspondence principle (Korrespondenzprinzip) and the application of the theory of astronomical perturbations to the calculation of the orbit of an electron—the complexity of these theories arises because we attempt to interpret atomic processes of the microcosmos on the basis of the “classical” laws of the macrocosmos, which are alien to that sphere of activity. We must approach these theories not so much from the point of view of the internal consistency and regularity, since all these theories are equally doomed to be displaced, but more from the point of view of their fruitfulness in discovering new simple facts and regularities, which will serve as the basis for a simple and systematic theory of the future. I say “simple” because the persuasiveness and simplicity of the laws of nature have always lain at the root of all scientific activity. From this perspective the quantum theory of atomic magnetism, as we have seen, has to its credit the Stern–Gerlach experiment, the simple interpretation of experimental results of magnetic measurements, the simple scheme of Sommerfeld, which relates the chemical and magnetic properties of the elements, and finally, a scheme, which, although not yet susceptible to interpretation, is by its nature extremely simple, and which binds together the magnetic “anomalies” (the multiplicity of the spectral lines, the Zeeman effect, and the magneto-mechanical effect). All these accomplishments are irrefutable and permanent assets, which not only confirm the existence of the theory itself, but lead us to anticipate that the concepts underlie the theory are correct ones, and that the further development of the the-

TABLE VI.

Number n of Bohr Magnetons	1	2	3	4	5
Apparent Number k of Weiss Magnetons According to the Initial Theory	8.7	13.7	18.7	23.7	28.7
The Same, According to the Corrected Theory (for $g=2$)	8.7	14.1	19.2	24.4	29.4

ory will lead to new advances and permit the creation of a fundamentally new and consistent theory of intraatomic processes.

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¹⁾For ferromagnetic objects the atomic moments are calculated from the saturation magnetization at low temperatures, while in paramagnetic materials there is no saturation.

²⁾As regards the historical sequence, it must be remarked that Weiss was the first to arrive at the concept of the magneton on the basis of his studies of the saturation of ferromagnets at low temperatures. This does not change the essence of the discussion.

³⁾The table is taken from the paper of Gerlach (Ref. a).

⁴⁾At the present time the authors of the theory acknowledge that the number of magnetons in an atom can be *half-integral* (multiplies of $1/2$)! (J. Phys. (Paris) 5, 129 (1924)).

⁵⁾Of course, with the choice of rational units for the angular momentum, equal to $h/2\pi$. See Eq. (4a).

⁶⁾I shall quote the simplest initial formula of Sommerfeld, without touching on the deeper and more productive analysis of this problem given by Bohr.

⁷⁾For $\cos \varphi$ we might even expect the value of k to be zero, which also corresponds to an integral (zero) value of the projection. However, using the adiabatic hypothesis, Bohr concluded that its value is $\cos \varphi=0$ exclusively (see the proof in e.g., Sommerfeld's *Atombau III Aufl.*, S. 382). On the basis of this reasoning this value was also not taken into account in the theory of Pauli. We shall not go into this issue, since the zero value $\cos \varphi=0$ is now considered as possible for *complex* atoms (the proof of Bohr is applicable only to hydrogen).

⁸⁾As is known, in this version the primary significance is attributed only to the emission events, whereas for *absorbing* systems a continuous set of states is permitted (continuous absorption).

⁹⁾The work of Stern and Gerlach was reported in detail in Usp. Fiz. Nauk SSSR 3(2–3), 301. (see also in the same issue the article of N. N. Semenov “Molecular beams”—Editor's note).

¹⁰⁾To eliminate the effect of collisions between the molecules.

¹¹⁾This circumstance was first pointed out independently by P. Epstein⁹ and W. Gerlach.¹⁰

¹²⁾In the most recent paper of Weiss (J. Phys. (Paris) 5, 129 (1924)) the new value $k=9$ was obtained for V'''' , which is in excellent agreement with the requirements of the theory. I have used this value in Table IV.

¹³⁾At high temperatures these metals become paramagnetic.

¹⁴⁾According to Sommerfeld,¹⁴ Cabrera believes that the magnetic moments of some ions of the iron group are measured so precisely that one can with certainty state that there is a discrepancy with the requirements of the quantum theory, while the theory of Weiss is supported. Despite all the authority of Cabrera in matters of this sort I nevertheless hold with Gerlach and Sommerfeld that to the unprejudiced mind the statement of the matter should be viewed in the opposite light, the more so since the numbers of Table III have the nature of a first approximation (the molecular fields are not taken into account; see also later the possibility of fractional numbers of Bohr magnetons in an atom).

¹⁵⁾As is known, for all multiple lines the Zeeman effect is anomalous in the sense that these lines are split not into three components as required by the classical and the elementary quantum theory, but into an extraordinarily large number (up to 24) components, with the spacing between the components and their polarizations also anomalous.

¹⁶⁾See text after Eq. 4(a) for the magnetomechanical anomaly.

¹⁷⁾Some statements of the first work of Sommerfeld, partially generalized in the third edition of his well-known book “*Atombau und Spektrallinien*”, were later somewhat modified by him.

¹⁸⁾The values of the quantum numbers corresponding to different states of the atom have been determined on the basis of a collection of spectral data. We cannot go into detail here, but later we shall regard these numbers as specified.

¹⁹⁾This function has the form

$$g = \frac{3}{2} + \frac{r(r+1) - k(k-1)}{2j(j+1)}$$

The number r is equal to zero for single lines, $1/2$ for doublets, $2/2$ for triplets, etc. The physical nature of the factor g is not presently known. It is hypothesized that the appearance of the factor g in Eq. (12) is due to the fact that the orientation of the individual electron orbits in a

magnetic field are to a known degree independent of one another. This assumption makes it possible to explain the nature of the magnetic splitting of the doublet spectral lines, but the application of this assumption to more complex structure has not been successful.

²⁰⁾ To characterize all the new developments in this field it is sufficient to say that previously our information did not go beyond triplets. Now it is possible to decipher the spectrum of Mn, which contains octets (eight lines). Some of its lines are split in a magnetic field into 24 components! All these complex relations are fully accommodated in the theoretical scheme of Landé.

²¹⁾ Here we can only touch upon this question in a superficial way. As is known, measurements of magnetomechanical effects makes it possible to determine the ratio between the angular momentum and the magnetic moment of the atom. The usual theory leads to relation (6) or (6a). The first experiments were in good agreement with this equation. However, a number of more precise experiments in recent years (Arvidson, 1920; Chattock, Susmith, Bates (1922)) have shown conclusively that expression (6a) cannot be applied directly to any of the investigated materials (Fe, Ni, the Heusler alloy) and that this expression must be replaced by the equation $m=2j$. The latter relation is a special case of our formula (12) for $g=2$. Most remarkable is the fact that Landé's spectroscopic theory of magnetism has yielded by entirely independent means the conclusion that $g=2$ for all atoms and ions in the normal single-quantum state (azimuthal quantum number $k=1$). Thus the magneto-mechanical anomaly can be "explained" on the basis of the assumption that the atoms or ions of a ferromagnetic substance under ordinary conditions are in a single-quantum state. Because of lack of space we must put to one side the question of how much this theory is compatible with the views of Bohr concerning the structure of the Periodic Table and the most recent investigations of the spectrum of iron vapor.

²²⁾ We are referring to the maximum multiplicity because the multiplicity of the energy levels of this atom, generally speaking, increases with the azimuthal quantum number k until the maximum value is attained. It is well known, for instance, that the single-quantum S energy levels (terms) generally are not split.

²³⁾ The number of "external" electrons is understood to mean the difference between the total number of electrons in a given atom and the number of electrons in the preceding inert gas.

²⁴⁾ See Sec. 5; Gerlach¹⁹ assumes that $n=5$ for Fe" and not $n=4$, and we do so also.

²⁵⁾ See also the note of Angerer and Joos in *Naturwissenschaften* for February 15, 1924.

²⁶⁾ This straight line is not found on the Sommerfeld diagram, but is

reproduced here from the arguments developed by Sommerfeld and published in the most recent of his papers.

²⁷⁾ For these laws see, e.g., Sommerfeld (Atombau. III Aufl. C. 6, § 6).

²⁸⁾ According to a verbal report of P. S. Ehrenfest, Oskar Klein, in calculating the action of a magnetic field on a hydrogen atom, concluded that the axis of the hydrogen atom is always perpendicular to the field. If the calculations of Klein are correct, then they are a serious argument in favor of the viewpoint of Landé.

²⁹⁾ The present-day theory, unlike the initial theory, allows for an alignment perpendicular to the field ($\cos \varphi=0$), if j is integral (see footnote 28), which is in complete accord with the quantization rules cited in the paper.

³⁰⁾ Landé has presented an interesting review of the fundamental difficulties that confront the modern theory of atomic magnetism.¹⁸

^a W. Gerlach, *Magnetismus und Atombau*, in "Ergibnisse der exakten Naturwissenschaften", II, 124 (1923).

^b A. Landé, *Fortschritte beim Zeemaneffekt*, *ibid.*, p. 147.

¹ P. Weiss, *Phys. Z.* **12**, 935 (1911); *Arch. Elektrotechnik.* **2**, 1 (1913).

² B. Cabrera, *J. de Phys.* **3**, 443 (1922).

³ A. Landé, *Phys. Z.* **20**, 228 (1919); *Verh. Dtsch. Phys. Ges.* **21**, 585 (1919).

⁴ W. Pauli, *Phys. Z.* **21**, 615 (1920).

⁵ O. Stern, *Z. Phys.* **7**, 249 (1921).

⁶ W. Gerlach and O. Stern, *Z. Phys.* **8**, 110 (1921); **9**, 349, 353 (1922).

⁷ A. Einstein and P. Ehrenfest, *Z. Phys.* **11**, 31 (1922).

⁸ A. Sommerfeld, *Ann. Phys. (Leipzig)* **70**, 32 (1923).

⁹ P. Epstein, *Science* **57**, 532 (1923).

¹⁰ W. Gerlach, *Phys. Z.* **24**, 275 (1923).

¹¹ A. Landé, *Z. Phys.* **5**, 231 (1921); **15**, 192 (1923); **19**, 112 (1923).

¹² A. Sommerfeld, *Ann. Phys. (Leipzig)* **63**, 112 (1920); *Z. Phys.* **8**, 257 (1922); *Ann. Phys. (Leipzig)* **70**, 132 (1923); *Ann. Phys. (Leipzig)* Nos. 3/4, (1924).

¹³ W. Heisenberg, *Z. Phys.* **8**, 273 (1922).

¹⁴ A. Sommerfeld, *Ann. Phys. (Leipzig)* **24**, 360 (1923); *Ann. Phys. (Leipzig)* Nos. 3/4, (1924).

¹⁵ A. Sommerfeld, *Z. Phys.* **19**, 221 (1923).

¹⁶ H. Gieseler and W. Grotrian, *Z. Phys.* **22**, 245 (1924).

¹⁷ A. Landé, *Naturwissenschaften*, **11**, 725 (1923).

¹⁸ A. Landé, *Phys. Z.* **24**, 441 (1923).

Translated by J. R. Anderson