INTRODUCTION TO THE THEORY OF MAGNETISM

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Classification of Magnetic Substances

WHEN a substance is placed in a magnetic field H, this field will induce inside the substance a field B which is given by

$$B = H + 4\pi M = \mu H.$$

Here M is the magnetisation of the substance and μ is its permeability. The magnetisation is due to the external field H. It is an empirical fact that, to a good approximation, M (with the exception of some special cases) is a linear function of H and we can put

$$M = \chi H$$

where χ is called the magnetic susceptibility. Susceptibility is a parameter characteristic of the substance considered, which, in general, depends on its temperature. According to sign and order of magnitude of χ substances are subdivided into three large classes:

I. $\chi < 0$	Diamagnetic substances.
II. $\chi > 0$	Paramagnetic substances.
III. $\chi = \infty$	Ferromagnetic substances.

Class I is largest as almost all organic molecules belong to it, as well as all noble gases, several metals such as the noble metals, bismuth, zinc, mercury, ... and non-metals such as sulfur, iodine, silicon, ... (Bates, 1961). In principle also all superconductors belong to this class, since below the transition point in a superconductor $B = 0$ (Meissner effect) so that $\chi = -1/4\pi$. Since, however, such a behaviour is due to quite different physical causes than normal diamagnetism, superconductors are not considered in this book. However, it should be mentioned that the "diamagnetic conception" of

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superconductors was important for the development of the theory of superconductivity (Bardeen, 1963).

The second class comprises all substances which possess a permanent magnetic moment, such as the transition elements of the periodic system and their compounds, as well as the rare earths, and the alkali metals, ...

A few substances belonging to Class II are ferromagnetic below a certain characteristic temperature, the Curie point; these substances represent Class III, which also comprises the antiferromagnetic and ferrimagnetic substances. The property of being ferromagnetic (antiferromagnetic, ferrimagnetic) is linked with definite crystalline structures so that this class comprises only solids.

The following treatment of the theories of magnetism is based on this classification of the substances.

I. Diamagnetism

1. The Bohr–van Leeuwen Theorem

In order to understand the fundamental effects of diamagnetism, one may be tempted first to develop a classical description and then to complete it with the necessary quantum-mechanical corrections. However, both diamagnetism and paramagnetism proved to be incomprehensible within the framework of an exact classical theory based on the magnetism of moving charges. This fact is sometimes called the Bohr–van Leeuwen theorem (Van Vleck, 1932a). If, for example, an electron with the charge e ($e = -e_0$; $e_0 = 4.8 \times 10^{-10}$ e.s.u.) is assumed to travel along a circular orbit (e.g. in a constant magnetic field), a magnetic moment m given by

$$m = \frac{j}{c} A = \frac{e}{2c} [r \wedge v]. \qquad (1.1)$$

will correspond to the circular current j obtained in this way; here c is the velocity of light, r the radius vector of the electron, v its velocity, and A is a vector, the magnitude of which is the area enclosed by the current and the direction of which is given by the right-hand rule. When the electron is assumed to move in the x, y-plane, only the z component of moment m will be non-zero:

$$m_z = \frac{e}{2c} (x\dot{y} - y\dot{x}).$$

This formula was given only to show that there is a linear relation between the magnetic moment and the velocity of the charge. This linearity remains unchanged even if we have complex trajectories and many electrons. Consider, for example, a system of N electrons which are described by their coordinates $q_1 \ldots q_{3N}$ and the corresponding canonical momenta $p_1 \ldots p_{3N}$. For this system the z component of

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the magnetic moment will be given by

$$m_z = \sum_{i=1}^{3N} a_i^z(q_1 \ldots q_{3N})\dot{q}_i, \qquad (1.2)$$

where a_i^z depends only on the position coordinates, q_i. The thermal mean of (1.2) is obtained when this function is provided with a weight factor (the Boltzmann function) and integrated over the whole of phase space:

$$M = \int m_z \frac{e^{-\mathscr{H}/kT}}{Z} dq_1 \ldots dq_{3N} dp_1 \ldots dp_{3N}. \qquad (1.3)$$

$\mathscr{H}$ is the Hamiltonian of the system generally given by

$$\mathscr{H} = \sum_{i=1}^{3N} \frac{1}{2m} \left(p_i - \frac{e}{c} A_i \right)^2 + eV(q_1, \ldots, q_{3N});$$

here m is the mass of the charge carriers, A is the vector potential, and V is the interaction potential. Z is the classical partition function,

$$Z = \int e^{-\mathscr{H}/kT} dq_1 \ldots dp_{3N},$$

k is Boltzmann's constant, and T is the absolute temperature. Substituting (1.2) in (1.3) we obtain

$$M = \frac{1}{Z} \sum_{i=1}^{3N} \int a_i^z(q_1, \ldots, q_{3N})\dot{q}_i e^{-\beta\mathscr{H}} dq_1 \ldots dp_{3N}; \qquad \beta = \frac{1}{kT}.$$

By virtue of the canonical equations of motion we have

$$\dot{q}_i = \frac{\partial\mathscr{H}}{\partial p_i}, \quad \dot{p} = -\frac{\partial\mathscr{H}}{\partial q_i},$$

and, integrating over the momenta, we obtain

$$M = \frac{1}{Z} \int \sum_{i=1}^{3N} a_i^z(q_1 \ldots q_{3N}) \frac{\partial\mathscr{H}}{\partial p_i} e^{-\beta\mathscr{H}} dq_1 \ldots dp_{3N}$$

$$= -\frac{1}{\beta Z} \int \sum_{i=1}^{3N} a_i^z(q_1 \ldots q_{3N}) \frac{\partial}{\partial p_i} e^{-\beta\mathscr{H}} dq_1 \ldots dp_{3N}$$

$$= -\frac{1}{\beta Z} \int \sum_{i=1}^{3N} a_i^z(q_1 \ldots q_{3N}) \left[e^{-\beta\mathscr{H}} \right]_{p_i=-\infty}^{p_i=+\infty} dq_1 \ldots$$

$$dq_{3N} dp_1 \ldots dp_{i-1} dp_{i+1} \ldots dp_{3N} = 0.$$

Thus we see that diamagnetism is not a classical but a quantum-mechanical effect; when the susceptibility formula is derived in a classical way, the derivation is always based on assumptions involving quantum-mechanical results in a more or less implicit form.

2. Diamagnetism of Atoms and Ions

The classical derivation of diamagnetic susceptibility according to Langevin (1905) and Pauli (1920) is based upon the assumption of an electron moving in a fixed orbit (frequency ω_0) around a nucleus, i.e. it is based on a quantum-mechanical assumption. In this case the centrifugal force and the Coulomb force acting on the electron must be in equilibrium. When the nuclear charge is equal to Ze_0 we have

$$m\omega_0^2 r = \frac{Ze_0^2}{r^2},$$

r being the distance between electron and nucleus. Hence we obtain for the orbital frequency

$$\omega_0 = \pm\sqrt{\frac{Ze_0^2}{mr^3}}.$$

If now a magnetic field H is applied parallel to the z-axis, the Lorentz force

$$F = \frac{e}{c}[v \wedge H]$$

will act on the electron in addition to the other forces. The condition of equilibrium for the forces in the plane perpendicular to the field is now given by

$$m\omega^2 r = \frac{Ze_0^2}{r^2} + \frac{e_0}{c}\omega r H,$$

where H is the magnitude of the magnetic field and ω is the orbital frequency of the electron, which has changed by ω_0.

This new frequency is given by

$$\omega = \omega_0\sqrt{1+\left(\frac{e_0 H}{2mc\omega_0}\right)^2} + \frac{e_0 H}{2mc}. \qquad (1.4)$$

With field strengths achievable in practice, $e_0 H/2mc$ is much smaller than ω_0 and we have in a good approximation

$$\omega = \omega_0 + \frac{e_0 H}{2mc} = \omega_0 + \omega_L.$$

Thus the application of the magnetic field has changed the orbital frequency by ω_L, which is usually called the Larmor frequency. This additional Larmor frequency gives rise to an additional current and an additional magnetic moment induced by the field. As there is an additional number, $\omega_L/2\pi$, of revolutions of the electron, per unit time, the current due to the Larmor frequency is given by

$$j = \frac{e\omega_L}{2\pi}.$$

The magnetic moment m_z induced by it will then be

$$m_z = \frac{j}{c} A = \frac{e\omega_L}{2\pi c} A.$$

Here A is the circular area bounded by the electron's orbit in the x, y-plane: $A = \pi(x^2 + y^2)$. Averaging over many identical electron orbits, we have

$$\overline{x^2} = \overline{y^2} = \overline{z^2} = \tfrac{1}{3}\overline{r^2},$$

r being the distance between electron and nucleus. Thus the magnetic moment of a diamagnetic substance consisting of N_0 identical atoms per cm³, each possessing one electron, will be given by

$$M = -N_0 \frac{e_0^2 H}{6mc^2} \overline{r^2}.$$

If several electrons are bound to the nucleus, in addition to the electrostatic interaction between electrons and nucleus, there will also exist an electrostatic interaction between the electrons. Since this interaction is spherical-symmetric, the Larmor theorem remains unchanged, as can be easily verified: the orbital frequency of each electron will be changed by ω_L. Hence it follows that in the case of

N_0 identical atoms with Z electrons the mean magnetic moment is given by

$$M = -N_0 \frac{e_0^2}{6mc^2} \sum_{i=1}^{Z} \overline{r_i^2} \cdot H, \qquad (1.5)$$

so that the susceptibility per unit volume is equal to

$$\chi_V = -N_0 \frac{e_0^2}{6mc^2} \sum_{i=1}^{Z} \overline{r_i^2}, \qquad (1.6)$$

and the atomic or molar susceptibility will be given by

$$\chi_A = -N \frac{e_0^2}{6mc^2} \sum_{i=1}^{Z} \overline{r^2}. \qquad (1.7)$$

N is the Avogadro number, equal to $6 \cdot 0022 \times 10^{23}$ mole^{-1}.

This calculation is based on the assumption of atoms which do not influence one another.

We have seen from the theorem by Bohr and van Leeuwen that a classical derivation of susceptibility will always be inconsistent. We therefore need a quantum-mechanical basis for eqn. (1.5).

The Hamiltonian of an atom with Z electrons in an external magnetic field is given by

$$\mathcal{H} = \frac{1}{2m} \sum_{i=1}^{Z} \left(p_i - \frac{e}{c} A(r_i) \right)^2 + \sum_{i=1}^{Z} U(r_i) + \frac{1}{2} \sum_{i \neq j} V(|r_i - r_j|).$$

Here $U(r_i)$ is the interaction of the ith electron with the nucleus and $V(|r_i - r_j|)$ is the ordinary electrostatic interaction between an electron at r_i and an electron at r_j. As these interactions are unimportant for what follows, we shall ignore them. The magnetic field is assumed to be constant, uniform, and parallel to the z-axis; the vector potential is then given by

$$A = \frac{H}{2}(-y, x, 0).$$

The expectation value of $\mathcal{H}$ is then obtained as

$$\mathcal{H} = \sum_{i=1}^{Z} \frac{\overline{p_i^2}}{2m} - \frac{eH}{2mc} \sum_{i=1}^{Z} \overline{(xp_y - yp_x)_i} + \frac{e^2 H^2}{8mc^2} \sum_{i=1}^{Z} \overline{(x^2 + y^2)_i}.$$

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Hence we obtain for the magnetic moment of the atom

$$\overline{m_z} = -\overline{\frac{\partial \mathcal{H}}{\partial H}} = \frac{e\hbar}{2mc} \sum_{i=1}^{Z} \overline{l_{zi}} - \frac{e^2 H}{4mc^2} \sum_{i=1}^{Z} \overline{(x^2+y^2)_i},$$

where

$$\hbar l_z = xp_y - yp_x$$

is the z-component of the orbital angular momentum of an electron, due to its motion around the nucleus. When the first term is different from zero, the atom has a permanent magnetic moment which is the cause of its paramagnetic behaviour, as this term as a rule exceeds the second, the diamagnetic term. As to the order of magnitude, in cgs units,

$$\hbar \overline{l_z} = m\overline{v}r \cong 10^{-27} \quad \text{and} \quad \frac{e_0}{c} H(\overline{x^2+y^2}) = \frac{2}{3} \frac{e_0}{c} H\overline{r^2} \cong 10^{-36} H,$$

i.e. for practical field strengths and usual electron orbit radii, the diamagnetic term can be neglected in the expectation value for the magnetic moment. Thus, the diamagnetism of an atom can only be measured if the atom has no permanent magnetic moment. It is well known that only atoms with closed shells, i.e. noble gases, satisfy this condition. (Although the expectation value of the angular momentum vanishes also for s-electrons, for example, the diamagnetism of an atom with one s-electron is masked by the weak paramagnetism of the spin of this electron.) For such electron configurations we therefore obtain for the mean magnetic moment of the atom

$$M = -\frac{e_0^2 H}{6mc^2} \sum_{i=1}^{Z} \overline{r_i^2}, \tag{1.5}$$

where we can put $\overline{x^2} = \overline{y^2} = \frac{1}{3} \overline{r^2}$ because of the spherical symmetry of the Hamiltonian. (In the case of a crystal this would be generally inadmissible.) Hence we obtain for the molar or atomic susceptibility as before

$$\chi_A = -N \frac{e_0^2}{6mc^2} \sum_{i=1}^{Z} \overline{r_i^2} \tag{1.7}$$

which is the same as the previous formula. It is an advantage of the quantum-mechanical derivation, compared with the classical derivation by Langevin, that it reveals the conditions under which the dia-magnetism of an atom can be observed, as the presence of closed shells cannot be understood within the framework of the classical concept. With the more exact derivation of eqn. (1.7), however, we did not achieve very much; the difficulties in the calculation of sus-ceptibility consist of the determination of the expectation values of r^2. The simplest case to be considered is that of a hydrogenic atom with nuclear charge Z.

If the electron is in a state with principal quantum number n deter-mining the energy of the electron, and the orbital quantum number, l, (because of spherical symmetry the magnetic quantum number plays no part), we obtain with the exact eigenfunctions of the hydrogen atom, according to Bethe and Salpeter (1957),

$$\overline{r^2_{n,l}} = \frac{a_B^2 n^2}{2Z^2}\{5n^2 + 1 - 3l(l+1)\},$$

where $a_B = \hbar^2/me_0^2 = 5\cdot29\times10^{-9}$ cm (Bohr radius); thus we obtain for the susceptibility

$$\chi_A = -N\frac{a_B^2 e_0^2}{6Z^2mc^2}n^4\left(\frac{5}{2} - \frac{3l(l+1)}{2n^2} + \frac{1}{2n^2}\right), \qquad (1.8)$$

i.e. χ is proportional to the fourth power of the principal quantum number. When we apply (1.8) to the ground state of the hydrogen atom ($n = 1, l = 0$) we obtain

$$\chi_A = -2\cdot38\times10^{-6} \text{ cm}^3/\text{mole.}$$

Because of the electron spin this result cannot be verified by experiment. It is, however, known empirically that in larger atomic complexes the spin becomes saturated; it was therefore tried to draw conclusions from measurements on organic substances about the susceptibility of the hydrogen atom. In this way Pascal (1920) obtained

$$\chi_A = -2\cdot93\times10^{-6} \text{ cm}^3/\text{mole.}$$

Although this result is rather satisfactory, other experimenters arrived at quite different values so that this method is not well suited to check the theoretical result.

The calculation of $\bar{r}^2$ for atoms with two or more electrons immediately entails considerable difficulties, which are due to the mutual influence of the electrons. An electron at a distance r from the nucleus (charge Z) is not exposed to the action of the whole nuclear charge but to this charge minus the electron charge inside the sphere of radius r around the nucleus, i.e. to $Z_{\text{eff}}(r) = Z - Z_{\text{el}}(r)$, where according to the usual laws of electrostatics, $Z_{\text{el}}(r)$ is given by

$$Z_{\text{el}}(r) = 4\pi \int\limits_0^r \varrho(r) r^2 \, dr,$$

where $\varrho(r)$ is the electron density at point r. (Here we tacitly assume a spherical-symmetric density distribution which strictly applies only to closed shells.) In a very rough approximation Z_{eff} can be replaced by a constant which will depend on the principal quantum number n and the orbital quantum number l (Van Vleck, 1932a):

$$Z_{\text{eff}} = Z - \sigma_{n,l}. \tag{1.9}$$

One could try to calculate the screening constants $\sigma_{n,l}$ (cf. Van Vleck, 1932a); in our rough approximation, however, it is better to take the screening constants as parameters to be obtained from, for example, the ground states of the atoms or ions, or their susceptibilities. In this case each electron in a shell with quantum numbers n and l moves in a Coulomb potential $Z_{\text{eff}} e_0 / r$ and, according to (1.8), $\bar{r}^2$ is obtained for this electron in the form of

$$\overline{r_{n,l}^2} = \frac{a_B^2 n^2}{2(Z-\sigma_{n,l})^2} \left(5n^2 + 1 - 3l(l+1)\right).$$

As each energy level displays a $2(2l+1)$-fold degeneracy, we have for an atom or ion with closed shells

$$\chi_A = -N \frac{a_B^2 e_0^2}{6mc^2} \sum_{n=0}^{n_{\text{max}}} \sum_{l=0}^{l_n} \frac{(2l+1) \cdot n^2 \cdot \left(5n^2 + 1 - 3l(l+1)\right)}{(Z-\sigma_{n,l})^2}, \tag{1.10}$$

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where the double sum is to be taken over all occupied states, i.e. the electron configuration of the atom or ion.

Another method of calculating $\bar{r^2}$ is based upon approximate analytical expressions for the radial part of the electron wave function which, besides the effective nuclear charge, also contains an effective principal quantum number n^*. (An effective quantum number is known to appear in the optical terms of the alkali metals; see, for example, Slater, 1960.)

Slater (1930; see also Angus, 1932) wrote the radial part in the form

$$\psi(r) \sim r^{n^*-1} e^{-\frac{Z-s_{n,l}}{n^*}\frac{r}{a_{B}}} \tag{1.11}$$

and gave simple rules as to the attribution of n^* and $s_{n,l}$ to the electron configurations in the atom (Slater, 1930; Angus, 1932). The form of (1.11) corresponds to the asymptotic behaviour of the hydrogen eigenfunctions for large distances from the nucleus, see, for example, the text by Landau and Lifshitz (1958).

Using (1.11) we then obtain

$$\overline{r_{n,l}^2} = \frac{a_{B}^2 (n^*)^2}{(Z-s_{n,l})^2} \left(n^* + \frac{1}{2}\right)(n^* + 1)$$

and for the molar susceptibility

$$\chi_{A} = -N \frac{a_{B}^2 e_0^2}{3mc^2} \sum_{n=1}^{n_{max}} \sum_{l=0}^{l_n} \frac{(n^*)^2 \left(n^* + \frac{1}{2}\right)(n^* + 1)}{(Z-s_{n,l})^2}. \tag{1.12}$$

The methods sketched in this way are more or less semi-empirical methods as the final formulas contain parameters obtained by choosing them in agreement with other data on the atom. Theoretically $\bar{r^2}$ can be calculated in three ways. One of them is the Thomas–Fermi method for statistical treatment of the atom (Gombás, 1956). The other two ways are the Hartree method and the Hartree–Fock method. Both are based on a variational principle for the electron wave functions with the approximation of replacing the interaction potential between the atomic electrons and all other electrons by its mean value averaged over all angles, where the still unknown wave functions are used in the averaging. In this way, we obtain from the Schrödinger

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equation for the many-electron problem an integro-differential equation which can only be solved numerically (Slater, 1960; Hartree, 1957). Unlike the Hartree method, the Hartree–Fock method takes the Pauli principle into account; for most atoms it is the best and most exact way of determining the physical quantities of an atom (Slater, 1960).

TABLE 1

Element	Exper. (Landolt-Börnstein, 1950)	Eqn. (1.10) (Van Vleck, 1932a)		Eqn. (1.12) (Slater, 1930)	Thomas–Fermi (Gombás, 1956)	Hartree (Stoner, 1929)	Hartree–Fock (Hartree and Hartree, 1938)
He	− 1·93	− 1·54	− 11·85	− 1·64	−	− 1·90	
Ne	− 7·2	− 5·7	−	− 5·6	− 12·8	− 8·6	
Ar	− 19·4	− 13·6	− 21·5	− 18·5	− 18·2	− 24·8	− 20·6
Kr	− 28	− 17·2	− 42	− 31	− 28·3		
Xe	− 43	− 25·4	− 66	− 47	− 47·3		

The table contains data on the atomic susceptibility $\chi_A \times 10^6$ mole/cm^3 for noble gases. The first values of the third column are the susceptibilities obtained with the theoretical screening constants; the second values of this column were obtained by means of empirical screening constants. The values of the fourth column were calculated according to Slater's rules.

Table 1 gives the molar susceptibilities of the noble gases as obtained by means of various methods and compared with the experimental results. With almost all elements the agreement between theoretical and experimental values is rather good.

The He atom is a special case since for this atom the wave function is known relatively exactly (Slater, 1960; Hylleraas, 1929; Kinoshita, 1957; Pekeris, 1958). The accuracy is essentially better than using the Hartree–Fock method. Using the results by Pekeris (1959; Stewart, 1963), for helium a value of $\chi_A = -1\cdot8905 \times 10^{-6}$ is obtained, while the experimental value obtained by Havens (1933) is

$$\chi_A = -(1\cdot906 \pm 0\cdot006) \times 10^{-6}$$

so that in this case we can speak of a very good agreement.

A comparison between theory and experiment is more difficult in the case of ions with noble-gas electron configurations (closed shells). First of all, the susceptibilities of these ions can only be measured in solutions or crystals, e.g. Na^+Cl^-, as these ions do not exist in the gaseous phase; secondly, there is a decisive uncertainty to be taken into account, which is due to the fact that the noble-gas configuration of ions is essentially less stable than that of the noble gases. Their susceptibility will therefore depend on the partner of the ion to be measured, on the structure of the crystal, or on the solvent. It is therefore difficult to conclude from the susceptibilities measured, the susceptibilities of the free ions which were calculated theoretically (Myers, 1952).

TABLE 2

Element	Exper. (Myers, 1952)	Eqn. (1.10) (Pauling, 1927)	Eqn. (1.12) Slater (see Myers, 1952)	Thomas-Fermi (Gombás, 1956)	Hartree (Hartree, 1928)	Hartree–Fock (Hartree and Hartree, 1938)
F^-	$-$ 9·4; $-12\cdot1$	$-$ 8·1	$-$ 8·1	$-24\cdot4$	$-17\cdot0$	
Cl^-	$-18\cdot3$; $-26\cdot5$	-29	$-25\cdot2$	$-34\cdot6$	$-41\cdot3$	$-30\cdot4$
Br^-	-30; -54	-54	$-39\cdot2$	$-51\cdot2$		
J^-	$-47\cdot7$; $-55\cdot4$	-80	$-58\cdot5$	$-63\cdot7$		
Li^+	$+$ 0·1; $-$ 6·7	$-$ 0·63	$-$ 0·7	$-$	$-$ 0·7	$-$ 0·7
Na^+	$-$ 5·25; $-12\cdot5$	$-$ 4·2	$-$ 4·1	$-$ 7·3	$-$ 5·6	$-$ 4·9
K^+	$-13\cdot4$; $-21\cdot1$	$-16\cdot7$	$-14\cdot1$	$-14\cdot4$	$-17\cdot3$	$-18\cdot3$
Rb^+	$-20\cdot4$; $-28\cdot2$	-35	$-25\cdot1$	$-26\cdot8$	$-29\cdot5$	
Cs^+	$-35\cdot1$; $-44\cdot3$	-55	$-38\cdot7$	$-37\cdot2$	$-47\cdot5$	
Mg^{++}	$-$ 1·6; $-13\cdot6$	$-$ 3·2	$-$ 3·1	$-$ 5·8	$-$ 4·2	$-$ 3·74
Ca^{++}	$-$ 4·5; $-18\cdot5$	$-13\cdot3$	$-11\cdot1$	$-$ 9·0	$-13\cdot1$	
Sr^{++}	-14; $-28\cdot5$	-28	$-21\cdot0$	$-21\cdot0$		
Ba^{++}	$-25\cdot3$; $-41\cdot1$	-46	$-32\cdot6$	$-30\cdot5$		

The table contains data on the atomic susceptibilities ($\chi_A \times 10^6$ mole/cm³) of some ions with noble-gas configurations. The second column gives the largest and smallest experimental values (after Myers). In the fifth column the susceptibility of Mg^{++} was calculated by Hirone (1935), and that of Ca^{++}, Sr^{++}, and Ba^{++} by Jensen (1936). The value for Mg^{++} in the seventh column was calculated by Yost (1940).

Naturally the values of χ compiled in Table 2 show a considerable spread. Given the spread in the experimental values we cannot say much about the agreement between theory and experiment. However, all theoretical methods yield a qualitative agreement.

3. The Fermi Gas

Passing over from substances whose atoms have a noble-gas configuration to the alkali metals, we see that the alkali ions also have noble-gas configurations; however, each of them has also an electron which, in the metallic state, is more or less separated from the atom. The appearance of free charges is a characteristic phenomenon of conductors and semiconductors. Like the ions they contribute to the magnetic behaviour of the substance. This behaviour depends partly on the temperature; in the following we shall therefore consider the thermodynamic properties of such an electron gas as far as they are essential for the magnetism. We shall neglect the electron–electron Coulomb interaction: this corresponds to the old Sommerfeld treatment of the electron gas in metals. (The influence of temperature on the diamagnetism of atoms and ions could be neglected because the noble-gas configuration is very stable and cannot be changed by temperature effects.) We now determine the (Helmholtz) free energy F of the electron gas with a given number of electrons and given energy:

$$F = E - TS. \tag{1.13}$$

Here E is the energy, T is the temperature, and S is the entropy. When the electrons are assumed to possess a discrete spectrum of states (marked by a subscript i), the energy is given by

$$E = \sum_i E_i \cdot f(E_i), \tag{1.14}$$

where E_i is the energy of the ith state and $f(E_i)$ is the mean number of electrons in this state. As in quantum mechanics, the subscript i characterises a whole set of variables determining the properties of the

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