A CALCULATION OF THE DIAMAGNETIC SUSCEPTIBLITY OF LI⁺, NA⁺ AND K⁺ FROM THOMAS-FERMI CHARGE DISTRIBUTION

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ABSTRACT. After giving a brief outline of the present theories of diamagnetism, the importance of the "electron subtraction" method for calculating the finite ion-radius is pointed out. The ionic radii of Li⁺, Na⁺ and K⁺ are calculated by this method graphically from Thomas-Fermi statistical charge distribution. Using the value of ρ_{ion} the values of χ_{M} for Li⁺, Na⁺ and K⁺ are then calculated. As compared with other theoretical values the results obtained by the author agree better with the experimental values. A useful and very simple curve tracer is also described.

INTRODUCTION

According to the classical theories of diamagnetism, the effect of a magnetic field (H), on a system composed of electrons in motion about a fixed nucleus, is equivalent (to a first approximation) to the imposition on the system, of a uniform rotation about the field direction (Larmor precession) with an angular velocity $2\pi\omega_{\text{n}} = \dfrac{eH}{2mc}$ where ω_{n} is the precessional frequency, other constants having the usual significance. This rotation of electorns produces a magnetic moment opposed to the field. The atomic diamagnetic susceptibility is given by the expression (Pauling (1927).

$$\chi_{\text{A}} = -\frac{e^2}{4mc^2}\sum_{k}r_k{}^2\sin^2\theta_k \qquad \ldots \quad (i)$$

where $r_k\sin\theta_k$ is the projection of r_k, the distance of the kth electron from the nucleus, normal to the field direction and $r_k{}^2\sin^2\theta_k$ is the time average of $r_k{}^2\sin^2\theta_k$. If the system under consideration has got an initial magnetic moment, both diamagnetic and paramagnetic effects are present, the magnitude of the latter being much greater. If the system, however, has initially zero magnetic moment, which is true for spherically symmetrical charge distribution of the closed-core type, there is no paramagnetic effect.

For systems with spherically symmetrical charge distribution, the quantum theory gives

$$r_k{}^2\sin^2\theta_k = 2/3\,r_k{}^2$$

thus

$$\chi_{\text{A}} = -\frac{e^2}{6mc^2}\sum_{k}\overline{r_k{}^2}$$

or $$\chi_{\text{M}} = -\frac{Le^2}{6mc^2}\sum_k \overline{r_k^2} = -2.83 \times 10^{10}\sum_k \overline{r_k^2} \qquad \ldots \quad (ii)$$

where L is the Avogadro's number.

Van Vleck (1932) and Pauling (*loc. cit.*) have calculated the expression for $\overline{r_k^2}$ from the new quantum mechanics. From the charge distribution conception of atoms, Pauling has calculated the diamagnetic susceptibility for inert-gas like configurations. The calculated values, however do not agree with the experimental values, probably due to some error in the determination of the screening constants.

A very useful method of computing the charge distribution in spherically symmetrical systems has been developed by Hartree (1928). The method, though very laborious and approximte, has been applied to a number of problems. Stoner (1934) has calculated the diamagnetic susceptibilities of a number of ions in the following manner.

If dN/dr denotes the radial charge density in electrons per unit radial distance

then $$\overline{r^2} = \int_0^x r^2\frac{dN}{dr}\, dr \Big/ \int_0^x \frac{dN}{dr}\, dr$$

as $\int_0^\infty \frac{dN}{dr}\, dr$ gives the total charge in the ion, the diamagnetic susceptibility from (ii) is

$$\chi_{\text{M}} = -2.83 \times 10^{10} \int_0^x r^2\frac{dN}{dr}\, dr \qquad \ldots \quad (iii)$$

Expressing the radial distance (r) in atomic units ($.528 \times 10^{-8}$ cm.)

$$\chi_{\text{M}} = -2.83 \times 10^{10}(.528 \times 10^{-8})^2 \int_0^x \rho^2 \frac{dN}{d\rho}\, d\rho$$

where $\rho = \frac{r}{a_0}$ and $a_0 = .528 \times 10^{-8}$ cm.;

hence $$\chi_{\text{M}} = -.790 \times 10^{-6} \int_0^x \rho^2 \frac{dN}{d\rho}\, d\rho \qquad \ldots \quad (iv)$$

Determination of the ionic radii and the calculation of χ

The values of χ (Table II) as determined experimentally from solutions or solid alkali halides, differ from those theoretically calculated from relation (iv) or those given by Slater, Pauling, etc. The difference is genuine, and may be accounted for on the following lines.

Goldschmidt (1940) has suggested that in alkali halide crystals the electronic charge of the ion is not extended to infinity but may be supposed to be present in a definite region. This 'rigid-sphere' concept, though not very sound, may be nearer to the actual state of affairs. In the present work the ionic radius ρ_{ion} (or the radius of the rigid sphere in Goldschmidt's words) has been determined by the "electron subtraction" method, used by J. N. Nanda (1945). This method has been preferred, on account of the fact that it takes into account the effect of the presence of the valence electron on the

charge in the ion. The effect of the neighbouring ions, however, has not been taken into account. The above idea, combined with the effect of the neighbouring ions, will be useful for the exact theoretical calculations of χ of the ions in crystals and also in solutions.

The ρ_{ion} is determined from the atomic field given by Thomas and Fermi (1928) using the electron subtraction method. Thomas-Fermi field has been used as it is easier and less laborious than other methods. From the statistical calculations, Fermi has shown that the number of electrons in an atom (At. No. $= Z$) is given by

$$\int_0^\infty \left(\frac{2mc^2}{\rho a_0}\chi'\right)^{\frac{3}{2}} \frac{8\pi}{3p^3} 4\pi\rho^2 a_0^3 d\rho$$

where ρ is in atomic units and χ is some function of ρ. Substituting the values of the constants the integral becomes

$$1.195 \int_0^\infty (\chi Z)^{\frac{3}{2}} \rho^{\frac{1}{2}} d\rho.$$
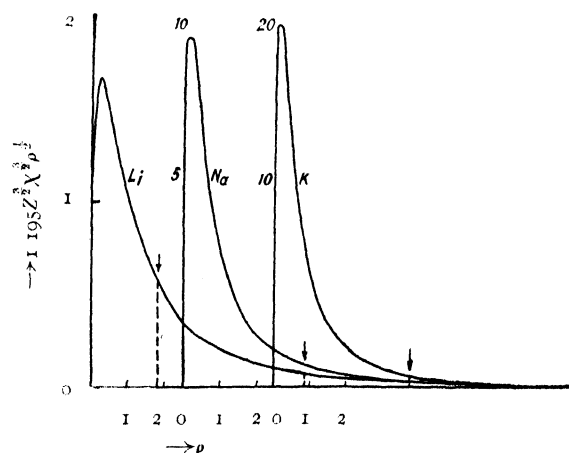
Thomas-Fermi charge distribution for Li, Na and K and their ionic radii ($\downarrow$) on electron subtraction method

Fig. 1

The integral is evaluated graphically by plotting between ρ and $1.195\chi^{\frac{3}{2}}Z^{\frac{3}{2}}\rho^{\frac{1}{2}}$ and, the region of the valence electron being determined from

$$1.195 \int_{\rho_{ion}}^{\rho = \infty} (\chi Z)^{\frac{3}{2}} \rho^{\frac{1}{2}} d\rho = 1$$

and ρ_{ion} determined from the graphs (Fig. 1). The ordinate scales for the three are different.

[While plotting these graphs on a big graph paper (56cm×43cm) it is found that it is very difficult to draw a smooth curve of such a length. The 'Frenchcurves' obtainable in the market are not of much use. Out of necessity a very simple curve tracer named (G.V.) was designed. A thin silicon steel strip about 40 cms. long 1.7 cms. wide and .034 cm. thick, cut from a transformer stamping is taken. A piece of lead sheet of the same length, 1.5 cms. wide and about .15 cm. thick is bent and fixed along the length of the strip, covering nearly .8 cm. of its width. A thin layer of lacquer polish is applied on lead (as otherwise the lead stains the graph paper and the hands) and the lower corners of the strip rounded. This, in simple, is the curve tracer. When a curve is to be drawn, the (G.V.) is bent to the proper shape of the curve and the curve traced. After use it is placed over a plane surface and straightened by simultaneouly pressing and rubbing it with the hand. This has saved much of my time and unnecessary trouble of rubbing].

The values of ρ_{ion} for Li^+ Na^+ and K^+ as determined by electron subtraction method are compared with those found by Goldschmidt (1940) and Huggins and Meyer by different methods (Table I).

TABLE I

Ionic Radii

No.	Ion	Ion		
		Goldschmidt	Huggins and Meyer	Electron* subtraction method
1	Li^+	.78 Å	.475 Å	.c85Å
2	Na^+	.98 Å	.875 Å	1.759 Å
3	K^+	1.35 Å	1.185 Å	1.996 Å

Now for the determination of χ_M Stoner has suggested that for ions in crystals and in solutions a limit will be imposed to the diamagnetically effective 'spread' of the charge distribution and we further suppose that the valence electron of the alkali atom, which is bound to the halide atom due to its electron—affinity, thus forming it a negative ion, is still equally effective on the remaining charge in the alkali ion, as it is in a free alkali atom. Hence therefore we shall consider the susceptibility integral for the total atom and restrict the integration to finite ρ_{ion}, thus in place of (iv) we have

$$\chi_M = .790 \times 10^{-6} \times 1.195 \int_0^{\rho_{ion}} (\chi Z)^{\frac{3}{2}} \rho^{\frac{5}{2}} d\rho.$$

The integral is evaluated graphically (Fig. 2). The ordinate scales are different and zero has been shifted. The values of χ_M as determined for Li^+, Na^+ and K^+

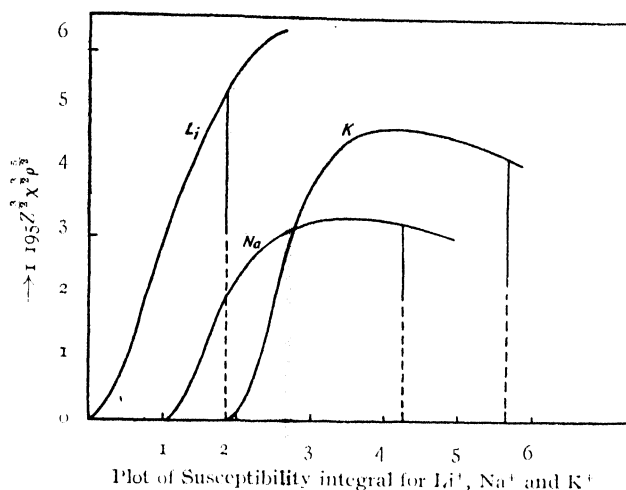Plot of Susceptibility integral for Li^+, Na^+ and K^+

Fig. 2

by the author are compared with the theoretical and experimental values obtained by others. (Table II, taken from Bhatnagar and Mathur (1935) to which the year of the previous work and the values calculated by the present author have been added.)

TABLE II

Gram-ionic Susceptibilities

Ion	Theoretical values				Experimental values			
	Pauling 1927	Stoner (Hartree) 1929	Slater (Brindly) 1931	Sharma 1945	Hocart 1929	Pascal	Kido 1932	Ikenmeyer 1929
Li^+	0.63	.70	.67	1.29	...	...	1.6	...
Na^+	4.2	5.47	4.2	10.89	$8.2 \pm .9$	7.6	7.6	10.4
K^+	16.7	17.64	14.4	19.06	$16.5 + 9$	16.0	13.6	16.9

The values obtained by the author agree better, especially for Li^+ and Na^+ with the recent experimental values.

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* These are ionic radii for free ions, only the field of the valence electron being taken into account.

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