The right side of Eq. (5.1) can be obtained from the expression on the right side of Eq. (5.2) by multiplying the latter by the factor.

$$[1+L^2/\eta^2][1+(L-1)^2/\eta^2]\cdots[1+1^2/\eta^2],$$

whose presence cannot be inferred from the consideration of limiting forms for $\eta\rightarrow\infty$. This factor can be checked, however, by collecting all terms in $\ln x$ which are present in the $K_\nu(x)$.

The result of the consideration is that the employment of Stirling's asymptotic expansion for $\Gamma'(i\eta)/\Gamma(i\eta)$ in the formula for Θ_L, ordering of all terms according to powers of $1/\eta^2$ with coefficients expressed as functions of $x=(8\rho\eta)^{\frac{1}{2}}$ gives a series which is identical with the series obtainable by evaluating the right side of Eq. (5). The series in the I_ν may be obtained either by means of Eq. (4) and Eq. (18) of [I] or by means of Eq. (33) of YWB.

The integral representation reproduced as Eq. (2) of the present paper applies also to attractive fields. The quantity $\Theta_L{}^{\mathrm{II}}$ may not be disregarded, however, in this case when one evaluates the coefficients of $1/\eta^{2s}$ in Θ_L because $e^{-\pi\eta}$ is infinite. The considerations do not apply, therefore, to attractive Coulomb Fields.

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Hartree Computation of the Internal Diamagnetic Field for Atoms*

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For an atom or monatomic ion in a magnetic field H there will be an induced shielding field $H'(0)$ at the the nucleus given by $H'(0)=(eH/3mc^2)v(0)$ where $v(0)$ is the electrostatic potential produced at the nucleus by the atomic electrons. Using the Thomas-Fermi model, Lamb put this expression into a calculable form. However, in modern nuclear induction and resonance absorption experiments it is important to have a more precise knowledge of the magnitude of this shielding field. In this paper computed values of $v(0)$ are given for all atoms and singly charged ions which have been treated by the Hartree or Hartree-Fock approximations to the self-consistent field method. By interpolation a list of $H'(0)/H$ values for all neutral atoms is given. Although it is impossible to check the accuracy of these values experimentally it is estimated from other evidence that they can be trusted to within five percent. An exception must be made, however, for the heaviest atoms where the relativity effect becomes appreciable, amounting to an estimated six percent correction to $H'(0)/H$ for $Z=92$. Finally, the usefulness of accurate values of the atomic shielding field in analyzing the total shielding field in molecules is discussed.

I. INTRODUCTION

In the case of an atom or monatomic ion in an external magnetic field H, Larmor's theorem states that the motion of the atomic electrons in the field is the same (neglecting terms in H^2) as the motion before the existence of the field, except for the superposition of the Larmor precession. This creates a shielding field at the nucleus which, although always small compared with the external field, constitutes an important correction in the measurement of nuclear magnetic moments by the resonance method. Lamb[1] derived an expression for this shielding field, showing it to depend directly on the electrostatic potential $v(0)$ produced at the nucleus by the atomic electrons. Evaluating $v(0)$ on the basis of the Thomas-Fermi model he obtained for the ratio of induced to external field

$$H'(0)/H=-0.319\times10^{-4}Z^{4/3}. \tag{1}$$

In the cases $Z=19$, 20, 26, 29, 37, 55, 74, and 80 where $v(0)$ was explicitly available from Hartree wave functions, Lamb showed that Eq. (1) is checked fairly well. This paper extends the computation of $v(0)$ and hence $H'(0)/H$ for all atoms and singly charged ions which have been treated by the Hartree or Hartree-Fock approximations to the self-consistent field method. The project was undertaken originally for a limited number of cases to determine the dependence of the shielding field $H'(0)$ on the state of ionization of an atom. The results indicated the possibility of just detecting a shift in nuclear resonance positions between an atom in a neutral and singly ionized state. However, with the subsequent discovery of larger shifts due to the effect of chemical binding (discussed below) it would be difficult to distinguish this small effect experimentally.

II. THEORY

Consider an atom with a spherically symmetrical charge distribution of radial charge density $\rho(r)$ in an external field H. As an element of volume we take a ring with axis passing through the nucleus and parallel to H, with cross section $rd\theta dr$ and perimeter $2\pi r\sin\theta$, so that its volume is $2\pi r^2\sin\theta d\theta dr$ and it will contain a

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[1] W. E. Lamb, Jr., Phys. Rev. 60, 817 (1941).

charge $\sin\theta d\theta dr\rho(r)/2$. The rotation of this charge ring with the Larmor frequency results in a current

$$di=[\sin\theta d\theta dr\rho(r)/2]eH/4\pi mc \qquad (2)$$

and by the Biot-Savart law the field $dH'(0)$ at the nucleus due to this current loop is

$$dH'(0)=(2\pi di\sin^2\theta)/rc. \qquad (3)$$

TABLE I. Values of $-v(0)$ for neutral atoms and singly charged ions computed from Hartree and Hartree-Fock wave functions.

Atomic number	$-v(0)$ in atomic units (a) without exchange	 (b) with exchange	Reference (a)	 (b)
1	1.000	1.000	a	a
2^+	2.000	2.000	a	a
2	3.37		b	
3^+		5.369		c
3	5.463	5.714	d	c
4	8.365	8.410	e	f
5		11.23		g
6	14.51	14.69	h	i
7		18.32		j
7^-		18.70		j
8^+	21.373	21.61	k	l
8	21.944	22.26	k	l
8^-		22.72		l
9		26.12		m
9^-	26.5	26.56	n	m
10		30.811		m
11^+	34.8	35.13	b	j
11		35.43		j
11^-		35.57		o
17^-	63.88	64.67	p	p
18	68.89	69.67	q	q
19^+	73.91	74.67	q	q
19		74.90		o
19^-		75.02		o
20^+		79.95		r
20	79.3	80.20	e	r
26	114.0		s	
29^+	133.5	135.1	t	t
30	139.3		u	
31^+	145.2		u	
31	146.5		u	
32	153.7		v	
33^+	160.0		u	
33	160.3		u	
37^+	187.5		n	
47^+	262		w	
55^+	323		x	
74	490		y	
80	543		e	

[a] Exact wave function.
[b] D. R. Hartree, Camb. Phil. Soc. Proc. **24**, 111 (1927–28).
[c] V. Fock and M. J. Petrashen, Physik. Zeits. Sowjetunion **8**, 547 (1935).
[d] J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1928–29).
[e] D. R. and W. Hartree, Proc. Roy. Soc. **149A**, 210 (1935).
[f] D. R. and W. Hartree, Proc. Roy. Soc. **150A**, 9 (1935).
[g] Brown, Bartlett, and Dunn, Phys. Rev. **44**, 296 (1933).
[h] C. C. Torrance, Phys. Rev. **46**, 388 (1934).
[i] A. Jucys, Proc. Roy. Soc. **173A**, 59 (1939).
[j] D. R. and W. Hartree, Proc. Roy. Soc. **193A**, 299 (1948).
[k] D. R. Hartree and M. M. Black, Proc. Roy. Soc. **139A**, 311 (1933).
[l] D. R. Hartree and B. Swirles, Phil. Trans. Roy. Soc. **238A**, 229 (1939-40).
[m] F. W. Brown, Phys. Rev. **44**, 214 (1933).
[n] D. R. Hartree, Proc. Roy. Soc. **151A**, 96 (1935).
[o] D. R. and W. Hartree, Proc. Camb. Phil. Soc. **34**, 550 (1938).
[p] D. R. and W. Hartree, Proc. Roy. Soc. **156A**, 45 (1936).
[q] D. R. and W. Hartree, Proc. Roy. Soc. **166A**, 450 (1938).
[r] D. R. and W. Hartree, Proc. Roy. Soc. **164A**, 167 (1938).
[s] M. F. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).
[t] D. R. and W. Hartree, Proc. Roy. Soc. **157A**, 490 (1936).
[u] W. and D. R. Hartree and M. F. Manning, Phys. Rev. **59**, 299 (1941)
[v] W. and D. R. Hartree and M. F. Manning, Phys. Rev. **59**, 306 (1941).
[w] M. M. Black, Mem. Manchester Lit. Phil. Soc. **79**, 29 (1935).
[x] D. R. Hartree, Proc. Roy. Soc. **143A**, 506 (1933–34).
[y] M. F. Manning and J. Millman, Phys. Rev. **49**, 848 (1936).

Substitution for di from Eq. (2) gives

$$\frac{H'(0)}{H}=\frac{e}{4mc^2}\int_0^\pi \sin^3\theta d\theta\int_0^\infty \frac{\rho(r)dr}{r}=\frac{e}{3mc^2}v(0). \qquad (4)$$

This is just the expression obtained by Lamb. For purposes of computation this may be written as

$$H'(0)/H=\tfrac{1}{3}\alpha^2 v(0), \qquad (5)$$

where α is the fine structure constant and $v(0)$ is now understood to be in atomic units and is of course a negative quantity.

In the self-consistent field method the approximation is made of spherical symmetry in the electronic distribution so that $v(0)$ can be computed simply. For carrying out the quadrature of $v(0)$ Simpson's "One-Third" rule was used. Suppose the definite integral of $f(x)$ over an interval of x from a to b is desired. Indicating the values of $f(x)$ at $x=a$ and at $x=b$ by y_0 and y_n and the intermediate values by y_1, y_2, $y_3\cdots$, Simpson's rule gives

$$I=\int_a^b f(x)dx=\tfrac{1}{3}h[y_0+4(y_1+y_3+\cdots+y_{n-1}) \\ +2(y_2+y_4+\cdots+y_{n-2})+y_n], \qquad (6)$$

where h is the value of the equal intervals between successive values of y. The quantity usually evaluated at successive intervals of r by the self-consistent field method is P or P^2, the latter being just the radial charge density $\rho(r)$ in atomic units if P is suitably normalized. Thus

$$y_m=(P_m{}^2/r_m)\bigg/\left(\int_0^\infty P^2dr\right). \qquad (7)$$

Table I gives the computed values of $-v(0)$. Considering the internal consistency of the data it is felt that the numerical integration does not introduce errors larger than 0.5 percent. In the first column a + or − sign after the atomic number signifies a positive or negative ion respectively. The second column lists the values of $-v(0)$ for atoms and ions whose wave functions have been calculated without taking account of exchange terms (Hartree approximation), and the third column lists values in those cases where exchange terms have been included (Hartree-Fock approximation). The fourth and fifth columns give the references for the wave functions used. This list of references should serve incidentally as a useful bibliography of wave functions obtained by the self-consistent field method.

Table II gives values of $H'(0)/H$ for neutral atoms. These values have been obtained using Eq. (5) with[2] $\alpha^2=5.3263\times10^{-5}$ and interpolating from Table I. As is seen from Table I, values of $v(0)$ with exchange for all neutral atoms up to and including Na are available

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[2] J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. **20**, 82 (1948).

(except for He in which case there are no exchange terms). For higher Z, values of $v(0)$ without exchange or for a singly charged ion often are the only ones available. That this introduces only a small error can be seen from Table I. Thus the values of $v(0)$ with exchange are on the average about one percent greater than the corresponding values without exchange, and the difference in $v(0)$ is 0.8 percent between Na and Na^+ and falls to 0.2 percent between As and As^+.

Figure 1 is a comparison of $H'(0)/H$ values for the light elements computed from Hartree-Fock wave functions and from Eq. (1) based on the Thomas-Fermi model.

III. DISCUSSION

Unfortunately there seems to be no way of determining $H'(0)$ experimentally since there is no way of stripping the atom of all of its electrons. Since the precision to which $H'(0)/H$ is known affects directly the precision to which a nuclear moment ratio can be quoted, an attempt will be made to estimate the accuracy of the values of $H'(0)/H$ listed in Table II.

Concerning the accuracy of wave functions obtained by the self-consistent field method the following evidence is available.

(1) The bulk diamagnetic susceptibility has been measured experimentally for most atoms and ions which have been treated by the self-consistent field method. The theoretical values from wave functions calculated without exchange tend to be lower than the experimental values by from 10 to 25 percent. However, when exchange terms are included the agreement is on the average good to within seven percent. The explanation for this is that the main contribution to the bulk diamagnetic susceptibility comes from the outer atomic electrons,[3] hence its value is quite sensitive to a contraction of the outer charge distribution which is the effect of adding exchange terms. On the other hand the electrostatic potential $v(0)$ of the atomic electrons is relatively insensitive to a change in the outer charge distribution so that its value is little affected by inclusion of exchange.

TABLE II. The internal diamagnetic correction for neutral atoms.

Z	$H'(0)/H(\%)$	Z	$H'(0)/H(\%)$	Z	$H'(0)/H(\%)$
1	0.0018	32	0.273	63	0.693
2	0.0060	33	0.285	64	0.709
3	0.0101	34	0.296	65	0.724
4	0.0149	35	0.308	66	0.740
5	0.0199	36	0.321	67	0.756
6	0.0261	37	0.333	68	0.772
7	0.0325	38	0.345	69	0.788
8	0.0395	39	0.358	70	0.804
9	0.0464	40	0.371	71	0.820
10	0.0547	41	0.384	72	0.837
11	0.0629	42	0.397	73	0.853
12	0.0710	43	0.411	74	0.869
13	0.0795	44	0.425	75	0.885
14	0.0881	45	0.438	76	0.901
15	0.0970	46	0.452	77	0.917
16	0.106	47	0.465	78	0.933
17	0.115	48	0.478	79	0.949
18	0.124	49	0.491	80	0.965
19	0.133	50	0.504	81	0.982
20	0.142	51	0.517	82	0.998
21	0.151	52	0.531	83	1.01
22	0.161	53	0.545	84	1.03
23	0.171	54	0.559	85	1.05
24	0.181	55	0.573	86	1.06
25	0.191	56	0.587	87	1.08
26	0.202	57	0.602	88	1.10
27	0.214	58	0.616	89	1.11
28	0.226	59	0.631	90	1.13
29	0.238	60	0.647	91	1.15
30	0.249	61	0.662	92	1.16
31	0.261	62	0.678		

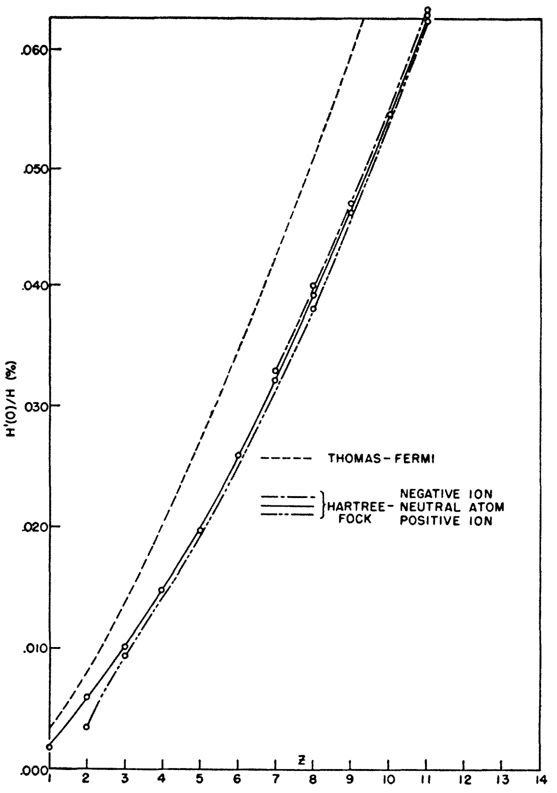

FIG. 1. Comparison of $H'(0)/H$ for the light elements, computed from the Thomas-Fermi model and from the Hartree-Fock model.

(2) X-ray and optical term values given by the self-consistent field method agree on the average to four percent with experimental values. If only the x-ray term values are considered the agreement is even better. Thus the self-consistent field method gives quite accurate energy values, *particularly for the inner electrons.*

(3) Hylleraas has carried out the calculation of $v(0)$ for He using his analytic He wave function. His final value $v(0)=-3.3764\pm0.0002$ is to be compared with $v(0)=-3.37$ from Table I.[4] Since the Hylleraas wave

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[3] Because of this fact an average agreement of seven percent is quite good. Diamagnetic susceptibilities are measured in the liquid or solid state where distortion of the outer electronic distribution by other atoms would be expected to be large.

[4] The author is indebted to Dr. H. L. Anderson for making available the results of this calculation by Professor Hylleraas. E. Hylleraas and S. Skavlem, Phys. Rev. 79, 117 (1950).

Table III. Contribution of outer electrons to the internal diamagnetic correction for atoms.

Atomic number	Electrons concerned	Percentage of total electrons	Percentage contribution to $H'(0)/H$
3	$2s$	33	6
4	$(2s)^2$	50	12
7	$(2p)^3$	43	14
9	$(2p)^5$	55	16
11	$3s$	9	0.8
19	$4s$	5	0.3
26	$(4s)^2$	8	0.6
31	$4p$	3	0.1
74	$(6s)^2$	3	0.1

function results in an energy for the helium atom differing by only 0.028 percent from the best experimental value, the excellent agreement between these values of $v(0)$ is another confirmation of the accuracy of self-consistent field energy values.

(4) X-ray scattering factors calculated from self-consistent field wave functions agree with experimental values to better than five percent in almost all cases. Since x-ray scattering depends mainly on the electronic distribution nearer the nucleus, this is a valuable indication of the accuracy of $v(0)$.

From the above considerations it would seem that the values of $H'(0)/H$ given in Table II could be trusted to about five percent. This estimate of the accuracy must however be qualified for the heaviest atoms due to the relativity effect which is generally not taken into account in self-consistent field calculations.[5] Since the inner shells are most affected by this correction it cannot be neglected. The heaviest atom for which it has been included[6] is Cu^+ where the value $v(0)=-134.3$ including relativity is to be compared with $v(0)=-133.5$ without relativity. Thus an increase of 0.6 percent occurs for $Z=29$. By approximate considerations it can be shown that the relativistic correction would be expected to go as Z^2 so that for $Z=92$ the correction would amount to about six percent of the computed value of $H'(0)/H$.

In recent nuclear induction and magnetic resonance absorption experiments it has been discovered that the value of the applied magnetic field H_0 for nuclear resonance at a fixed radiofrequency may depend on the chemical compound containing the resonating nucleus.[7–9] Ramsey[10] subsequently obtained a formal expression for the total magnetic shielding field in molecules, showing it to consist of two terms. The first is a simple diamagnetic term identical with the term for atoms except that the integration is extended over all the electrons in the molecule rather than only the one atom containing the resonating nucleus. The second is a second-order paramagnetic term which depends on the wave functions of all the excited states of the molecule. Ramsey gives a method of calculating the contribution of this term for linear molecules.

Accurate knowledge of the atomic diamagnetic correction is of value for two reasons. First, in those experiments in which the nucleus is contained in a free atom or in a monatomic ion rather than in an atom bound in a molecule or ionic complex, the atomic diamagnetic correction can be applied directly. Thus for aqueous solutions of *some* salts and for monatomic gases such as He^3 and $Xe^{129,131}$ this would be the case. Second, the self-consistent field computations give not only the most accurate evaluation now possible for the atomic diamagnetic correction but also information as to the relative contributions of the different electronic shells to this term. From Table III it is seen that the outer or valence electrons give a very small contribution to $H'(0)/H$. This of course would be predicted due to the $1/r$ behavior of $v(0)$.[11] Thus it would be expected, except perhaps for the lightest atoms, that molecular perturbations of the outer electrons would have little effect on $H'(0)/H$ and that contributions to $v(0)$ from electrons belonging to other atoms of the molecule would be relatively small. Hence to a first approximation the diamagnetic term in Ramsey's expression for the molecular shielding can be replaced by the value of $H'(0)/H$ from Table II for the atom concerned. This simplifies matters considerably. The observed shifts of nuclear resonances from one molecule to another are often as large as, or greater than, the entire atomic diamagnetic correction for the atom concerned.[12] The diamagnetic field at the nucleus for both molecules would be closely the same and hence the shift must be attributed chiefly to a *difference* in the second-order paramagnetic field in the two molecules. In particular, when a difference of resonance position is measured between a nucleus in an ion or atom and the same nucleus in a polyatomic molecule, the field difference would be entirely attributed to a second order paramagnetism in the molecule. Of course when an observed shift between two molecules is *small* compared to the atomic internal diamagnetic field for the atom containing the resonating nucleus, it could well be due to a difference in the diamagnetic term, the second-order paramagnetism being essentially the same for both molecules.

The writer wishes to express his thanks to Dr. L. C. Biedenharn, Jr. for several valuable discussions about this work.

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[5] The spin-orbit coupling correction which is also not taken into account would alter the wave functions of the outer electrons slightly, but would be expected to have a negligible effect on $v(0)$.

[6] A. O. Williams, Jr., Phys. Rev. **58**, 723 (1940).

[7] W. D. Knight, Phys. Rev. **76**, 1259 (1949). The bulk of this letter is concerned with the nuclear magnetic resonance shift in metals. However, a brief mention is made of the observation of shifts among some phosphorous compounds.

[8] W. G. Proctor and F. C. Yu, Phys. Rev. **77**, 717 (1950).

[9] W. C. Dickinson, Phys. Rev. **77**, 736 (1950).

[10] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

[11] For comparison, the contribution of the $(1s)^2$ shell to $v(0)$ varies from 44 percent for $Z=26$ to 30 percent for $Z=74$.

[12] Experimental data on second-order paramagnetic shifts for several elements will be given in a forthcoming paper.