Statistical Atom with Angular Momentum*

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(Received July 12, 1954)

By means of a variational principle, the method of Thomas and Fermi is extended, in a semiclassical manner, to atoms with a net total angular momentum. The resulting equation for the potential, which is valid for large angular momentum, is solved for small angular momentum, yielding approximate charge and current distributions for atoms in P and D states. Orbital magnetic hyperfine structure, and electric quadrupole hfs are calculated as a function of atomic number, and it is shown that the first is in approximate agreement with experiment.

I. INTRODUCTION

THE method of Thomas[1] and Fermi[2] yields an approximate charge distribution for atoms with no net angular momentum. This method, because of statistical approximations and inexact treatment of quantization rules, is valid in the limit of large atomic number (implying a large number of electrons and high quantum numbers). In this limit, however, it is more accurate than the single-particle Hartree[3] method, for the statistical model is completely self-consistent, whereas the Hartree method assumes separability of the angular coordinates.

Certain atomic properties are particularly sensitive to the amount of correlation between electrons. In particular, the quadrupole coupling constant q can be related to the magnetic hfs coupling constant, if it is assumed that the last electron moves in a spherically symmetric potential caused by the nucleus and core of electrons.[4] Corrections to this, due to electron correlation, have been calculated by Sternheimer[5] starting from the Hartree single-particle model.

It was suggested by Rabi[6] that a completely self-consistent statistical model for an atom with angular momentum might, in the appropriate limit, be more accurate than the Hartree model, since it would include angular correlations and thus give immediately a result corresponding to the quadrupole shielding effect found by Sternheimer by a perturbation calculation. This paper is devoted to the treatment of the statistical model with a net total angular momentum.

In Sec. II, starting from a variational principle for the total energy of the atom, while keeping the total number of electrons and total angular momentum constant, we obtain a differential equation for the potential. It is then shown that this equation corresponds to uniform rotation of the atom as a whole.

In Sec. III we solve the previously mentioned equation approximately, and use the resulting solution to compute the magnetic field at the nucleus due to electron motion. This is in fair agreement with experiment. A corresponding calculation of q is in disagreement with Sternheimer's results. We will show that the statistical model is invalid for calculating phenomena of this type. The reason for this is that the statistical model (with its inexact treatment of quantization rules) leads to an atom model in which an excessive degree of configuration interaction has taken place. As a result the charge symmetric characteristics of actual atomic states have been lost, although the magnetic properties are affected to a much smaller degree.

Atomic units ($\hbar=m=e=1$) are employed throughout the paper.

II. DERIVATION OF THE BASIC EQUATION

As a starting point, we must determine the distribution of electrons in momentum space at some arbitrary point in configuration space. If these electrons are to have some net angular momentum about the origin, then they must have some net linear momentum. Clearly this can be best accomplished by displacing the usual spherical distribution of a totally degenerate electron gas ($T=0$) by an amount $\mathbf{D}$, as indicated in Fig. 1. This obvious result may easily be obtained formally, by the proceedures well known in statistical mechanics for maximizing the probability of the configuration in phase space.[7] One must simply add the constraint of a nonvanishing total angular momentum, to the usual constraints of total number and total energy.

The procedure now consists of evaluating the total energy of the atom, assuming that the atom consists of

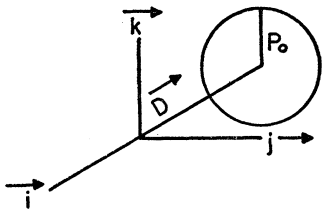

FIG. 1. Distribution of electrons in momentum space at some arbitrary point of configuration space.

* Supported in part by a grant from the National Science Foundation.

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[1] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).
[2] E. Fermi, Z. Physik **48**, 73 (1928).
[3] D. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928).
[4] Davis, Feld, Zabel, and Zacharias, Phys. Rev. **76**, 1076 (1949).
[5] R. Sternheimer, Phys. Rev. **84**, 244 (1951).
[6] I. I. Rabi (private communication).
[7] R. W. Gurney, *Introduction to Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 35.

completely degenerate electrons whose configuration is specified by $\mathbf{D}(\mathbf{r})$ and $P_0(\mathbf{r})$. The total energy is then minimized subject to two constraints, namely that the total number of electrons is N, and the total angular momentum is J. The angular momentum is treated classically, and J_z is taken equal to J.

$$\mathcal{E}_k=\frac{2}{(2\pi\hbar)^3}\int d\mathbf{r}\int_{\text{sphere}} d\mathbf{p}\frac{p^2}{2m}=\int d\mathbf{r}\left[\frac{P_0{}^5}{10\pi^2}+\frac{P_0{}^3D^2}{6\pi^2}\right], \quad (1)$$

$$\mathcal{E}_P=\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\int d\mathbf{r}n(\mathbf{r})V_N(\mathbf{r}), \quad (2)$$

where

$$n(\mathbf{r})=\frac{2}{(2\pi\hbar)^3}\int_{\text{sphere}} d\mathbf{p}=\frac{1}{3\pi^2}P_0{}^3, \quad (3)$$

V_N=potential of the nucleus,

$$N=\int d\mathbf{r}n(\mathbf{r}), \quad (4)$$

and

$$\mathbf{J}=\int d\mathbf{r}\mathbf{r}\times\mathbf{D}(\mathbf{r})n(\mathbf{r})=\int d\mathbf{r}D(\mathbf{r})r\sin\theta n(\mathbf{r}) \quad (5)$$

[where (r,θ,φ) are spherical polar coordinates]. We have anticipated the result and set $\mathbf{D}(\mathbf{r})$ in the $\boldsymbol{\theta}_0$ direction. We now eliminate the variable $P_0(\mathbf{r})$ in favor of $n(\mathbf{r})$, and introducing the Lagrangian multipliers λ and μ, we have for the quantity to be minimized

$$\mathcal{E}=\int d\mathbf{r}\left\{\frac{(3\pi^2)^{5/3}}{10\pi^2}n^{5/3}+\frac{D^2n}{2}\right\}+\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}$$
$$-\int d\mathbf{r}n(\mathbf{r})V_N+\lambda\int d\mathbf{r}rD\sin\theta n(\mathbf{r})+\mu\int d\mathbf{r}n(\mathbf{r}). \quad (6)$$

A straightforward variation with respect to D yields

$$D(\mathbf{r})=\lambda r\sin\theta. \quad (7)$$

Variation with respect to $n(\mathbf{r})$, with the double integral in the potential energy taken into account, yields

$$-\frac{\lambda^2r^2\sin^2\theta}{2}+\frac{5}{3}\frac{(3\pi^2)^{5/3}n^{\frac{2}{3}}}{10\pi^2}-\varphi+\mu=0, \quad (8)$$

where

$$\varphi(\mathbf{r}')=V_N-\int d\mathbf{r}\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}=\text{potential at }\mathbf{r}'. \quad (9)$$

We eliminate $D(\mathbf{r})$ and solve for $n(\mathbf{r})$. Invoking Laplace's equation, we obtain

$$\nabla^2\varphi=\frac{4}{3\pi}\{2(\varphi-\mu)+\lambda^2r^2\sin^2\theta\}^{\frac{3}{2}}, \quad (10)$$

with the boundary conditions that

$$\text{and}\qquad \begin{aligned} r\varphi&\longrightarrow z \quad \text{as} \quad r\longrightarrow 0,\\ r\varphi&\longrightarrow 0 \quad \text{as} \quad r\longrightarrow\infty. \end{aligned} \quad (11)$$

The parameters λ and μ are determined through Eqs. (4) and (5).

Examination of $D(\mathbf{r})=\lambda r\sin\theta$ shows that the model corresponds to a rigid sphere rotating uniformly with angular velocity λ. The associated centrifugal potential is $\frac{1}{2}\lambda^2r^2\sin^2\theta$, which makes the effective potential at a point $\mathbf{r}$:

$$\varphi_{\text{electric}}+\tfrac{1}{2}\lambda^2r^2\sin^2\theta. \quad (12)$$

Thus we see that Eq. (10) can be obtained immediately from the usual Thomas-Fermi equation with the insertion of this effective potential. We have established the interesting fact that a statistical atom with angular momentum rotates as a whole.

III. APPROXIMATE SOLUTION AND APPLICATIONS

We are interested in atoms in P states ($J=1$), and hence λ small. Thus we may solve Eq. (10) by a perturbation method. Expanding the right-hand side in powers of λ^2 and μ, we obtain

$$n(\mathbf{r})=\frac{1}{3\pi^2}(2\varphi)^{\frac{3}{2}}+\frac{1}{2\pi^2}(2\varphi)^{\frac{1}{2}}(\lambda^2r^2\sin^2\theta-2\mu). \quad (13)$$

Let

$$\text{and}\qquad \begin{aligned} n(\mathbf{r})&=n_0(r)+\lambda^2n_1(\mathbf{r})\\ \varphi(\mathbf{r})&=\varphi_0(r)+\lambda^2\varphi_1(\mathbf{r}), \end{aligned} \quad (14)$$

where φ_0 satisfies

$$\nabla^2\varphi_0(r)=\frac{4}{3\pi}(2\varphi_0)^{\frac{3}{2}}=4\pi n_0, \quad (15)$$

and is the well-known[8] solution to the Thomas-Fermi equation. From Eqs. (4) and (7),

$$J=\lambda\int r^2\sin^2\theta n(\mathbf{r})d\mathbf{r}. \quad (16)$$

Thus we may set $n(\mathbf{r})=n_0(r)$ in Eq. (16), and obtain λ directly with a relative error of only λ^2 (typically $\lambda=0.03$). By the well-known change of variables this may be put in universal form, i.e., the atomic number Z may be eliminated.

Inserting Eq. (14) into Eq. (10) we obtain

$$\nabla^2\varphi_1-\frac{4}{\pi}(2\varphi_0)^{\frac{1}{2}}\varphi_1=\frac{2}{\pi}(2\varphi_0)^{\frac{1}{2}}(\lambda^2r^2\sin^2\theta-2\mu), \quad (17)$$

which is an eigenvalue equation for μ. We thus have

$$n_1(\mathbf{r})=\frac{1}{\pi^2}(2\varphi_0)^{\frac{1}{2}}\varphi_1+\frac{1}{2\pi^2}(2\varphi_0)^{\frac{3}{2}}(\lambda^2r^2\sin^2\theta-2\mu). \quad (18)$$

[8] V. Bush and S. H. Caldwell, Phys. Rev. **38**, 1898 (1931).

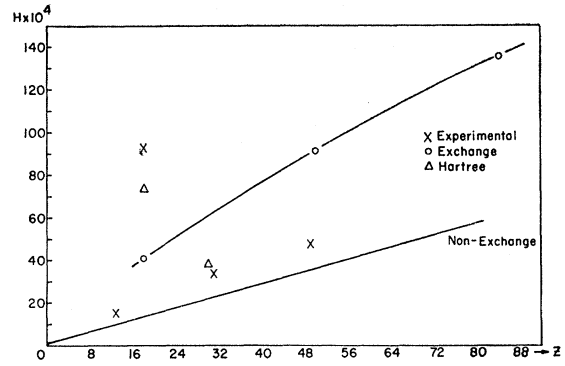

FIG. 2. Magnetic field at the nucleus, due to electron orbital motion, as a function of atomic number.

In order to get a more accurate result, the theory and calculations were repeated including exchange.[9] φ_0 now has the property of being zero outside of a cut-off radius r_0. In the perturbation analysis we assumed that r_0 did not change with the introduction of angular momentum. Allowing for a change in r_0 is possible,[10] but rather complicated. Including this effect would not affect the magnetic hyperfine coupling, nor would it change the results for the quadrupole coupling in an essential way. For the theory with exchange the equation cannot be put in to universal form, and numerical calculations were carried through for $Z=18$, $Z=50$, and $Z=84$.[11]

In order to compare with experiment, we calculated the magnetic field at the nucleus due to the orbital motion of the electrons.

$$H=\frac{e}{2mc}\int\frac{\mathbf{j}(\mathbf{r})\times\mathbf{r}}{r^3}d\mathbf{r}. \tag{19}$$

Thus, with negligible error

$$H=\frac{8}{9\pi}\left(\frac{\lambda}{137}\right)\int_0^\infty(2\varphi_0)^{\frac{3}{2}}rdr. \tag{20}$$

This gives, in the nonexchange approximation,

$$H=ZJ(0.73\times10^4)\text{ gauss}. \tag{21}$$

This, as well as values including exchange, and values obtained from the Hartree method, are compared with experimental values (obtained from $\Delta\nu$ and known nuclear magnetic moments) in Fig. 2. Note how the statistical method averages the effect of shell structure.

The quadrupole coupling constant q is given by

$$q=\int P_2(\cos\theta)n(\mathbf{r})d\mathbf{r}/r^3. \tag{22}$$

For $Z=18$, φ_1 was evaluated and shown to contribute to q an amount of the same order of magnitude as the contribution of the second term in Eq. (18). Using only this second term, we obtain in the nonexchange approximation

$$q=-\frac{27\pi J^2}{80}\frac{\int(2\varphi_0)^{\frac{3}{2}}rdr}{\left[\int(2\varphi_0)^{\frac{3}{2}}r^4dr\right]^2}. \tag{23}$$

The integral is weakly divergent at large r, and must be cut off at a reasonable value, yielding

$$q=-(J^2/Z^{\frac{4}{3}})(0.002). \tag{24}$$

For the model with exchange, in the same approximation

$$q_{18}=-2.2\times10^{-3},\quad q_{50}=-9.0\times10^{-4},\quad\text{and}\quad q_{84}=-4.5\times10^{-4}. \tag{25}$$

It will be observed that these values are two orders of magnitude smaller than Sternheimer's results.

That this is reasonable may be seen by noting that the statistical model does not take into account properly the spatial charge distribution associated with quantum-mechanical angular momentum. The statistical atom model can not hope to yield properties which vary in the characteristic way of the Periodic Table, even though one has explicitly inserted the proper angular momentum. In particular, q changes sign in actual atoms according as one considers atoms with one more or one less electron than corresponds to a closed shell. The magnetic properties do not behave in this manner, since the connection with angular momentum is more direct. (We may note how the atomic magnetic moment is given directly by the angular momentum, whereas the atomic quadrupole moment is only indirectly related to the angular momentum.)

[9] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).
[10] P. Gombás, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer Verlag, Berlin, 1949), p. 79.
[11] We are indebted to Dr. L. H. Thomas who kindly supplied us with solutions to the statistical atom with exchange.