proper Z dependence in two electron atoms. The absolute difference of the curves in Fig. 1 is not large. This much difference might well be expected from the type of potential and wave function used in this calculation where the purpose was to test the Z dependence of a particular type of correlational potential.

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Model for the Statistical Atom with Nonvanishing Angular Momentum*

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In the first of the coupled integro-differential equations satisfied by the Green's functions of the many-body system the Hartree–Fock approximation is made for the two-particle Green's function. The resulting equation is written in a mixed position-angular momentum representation in such a way that use may be made of whatever empirical information about the angular momentum of the system is available. In the mixed position-angular momentum representation the one-particle Green's function appears as a sum of terms each of which corresponds to a different value of the angular momentum. For the principal groups of the periodic table in which the angular momentum of the atom is carried by either one, two, or three electrons added to or missing from a closed shell the appropriate terms in the expression for the one-particle Green's function are identified. The first of the coupled integro-differential equations for the Green's functions is then solved to lowest order in $\hbar$ in the manner indicated by Baraff and Borowitz. The result is a modified Thomas–Fermi model that differs from the previous results of Sessler and Foley for the same problem. The Sessler–Foley modification of the Thomas–Fermi atom is rederived in the spirit of the cranking model for the nucleus by spinning the potential. The present formalism is seen to lead to the Sessler–Foley result in the limit of many particles carrying the angular momentum. However, the region of validity of the cranking model in the nucleus lies far removed from the magic numbers where there are many nucleons outside a spherical core. Thus, the Sessler–Foley result may be interpreted as a kind of cranking model of the atom. In contrast to the previous work the present formalism yields a sign change for the quadrupole coupling constant on passing through closed shells and calculated values for the quadrupole coupling constant of the halogens are seen to be within an order of magnitude of the accepted values.

I. INTRODUCTION

THE model of Thomas[1] and Fermi[2] allows one to calculate a density distribution of electrons in an atom by assuming that at each point in the atom, the electrons constitute a degenerate Fermi gas. The energy of the system is written in terms of the density and minimized subject to the condition that the number of electrons is constant. One is naturally led to ask about the utility of this model for describing other properties of the atom, for example, the angular momentum.

One suspects that a straightforward inclusion of angular momentum in the Thomas-Fermi model will lead to unsatisfactory results. For one thing, the assumed density in momentum space in this model is symmetric with respect to the origin. It thus possesses no net linear or angular momentum. For another, the only angular momentum in a statistical system compatible with a fixed energy is a rigid rotation about a fixed axis. This model is at variance both with the assumed density and with the known angular momentum distribution in real atoms.

To overcome the first (but not the second) difficulty, Sessler and Foley[3] were led to displace the distribution in momentum space from the origin by a position-dependent amount. This assumption used in the procedure similar to the original derivation of the Thomas-Fermi model yields a spherical atom spinning rigidly about a fixed axis.[4] This result may also be derived by spinning the nuclear potential in analogy to the nuclear cranking model of Inglis.[5,6]

A satisfactory approach might be to restrict the phase-space density in the statistical model to a fixed energy and total value of the angular momentum. This is a difficult problem in the conventional formulation of the Thomas-Fermi model. Recently, however, Baraff and Borowitz[7] have derived the Thomas-Fermi model of the atom from the many-body Schrödinger equation

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[1] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[2] E. Fermi, Z. Physik **48**, 73(1928).

[3] A. M. Sessler and H. M. Foley, Phys. Rev. **96**, 366 (1954).

[4] See, for example, L. Landau and Ya. Smorodinsky, *Lectures on Nuclear Theory* (Plenum Press, New York, 1959), Chap. 6 for an ample discussion of the fact that a spherical quantum mechanical system cannot rotate.

[5] D. Inglis, Phys. Rev. **96**, 1059 (1954).

[6] D. Inglis, Phys. Rev. **97**, 701 (1955).

[7] G. A. Baraff and S. Borowitz, Phys. Rev. **121**, 1704 (1961).

using Green's function techniques. One can modify this derivation to restrict the phase-space density allowing only specified values of the total angular momentum of the system.

In this derivation one uses the Green's function hierarchy equations in the Hartree-Fock approximation. In order to describe a statistical atom with angular momentum in this method, an appropriate representation for the Green's functions is introduced. In this representation the Green's functions appear as infinite sums over all angular momenta of partial Green's functions. One can then isolate the significant terms in the sums corresponding to the case of a few electrons carrying the angular momentum of the system outside a spherical core and to the case of the angular momentum being distributed among all the electrons in the atom. The last mentioned case yields the Sessler-Foley result as it should being a completely statistical calculation.[8]

Some numerical calculations of quadrupole coupling constants are given for comparison with similar calculations by Sessler and Foley.

II. SESSLER-FOLEY MODEL

In their work Sessler and Foley arrive at the conclusion that a statistical atom with angular momentum rotates as a whole. This result is consistent with a theorem proven by Landau and Lifshitz[9] that states that the only macroscopic motions compatible with an equilibrium state of a statistical system are translation with a uniform velocity and rotation with uniform angular velocity about a fixed axis.

This result depends on the fact that we have no knowledge of the internal distribution of angular momenta; we know only its total value. One might, therefore, anticipate a different result if one knew on empirical grounds that the entire angular momentum of the system was carried by a single particle. This, then, would correspond to a further restriction of the volume in phase space available to the microcanonical ensemble. We shall indeed find that one is led to different equations for the density in the system when one inserts empirical conditions known to hold. Indeed, even without the inserting of empirical information, a detailed treatment allowing for internal degrees of freedom can be made leading to different results than those illustrated above.[10]

It would therefore seem reasonable to find that the statistical atom with only the value of the total angular momentum specified should rotate rigidly as indeed was found by Sessler and Foley. These workers introduced an angular momentum into the Thomas-Fermi atom where it is ordinarily absent by displacing the Fermi sphere in momentum space from the origin by a position-dependent amount $\bar{D}(\mathbf{r})$. This imparts a net linear momentum to each point in the atom and a nonzero angular momentum is now possible.

The resulting equation for the potential energy in the atom is

$$\nabla^2\Phi = (4e^2/3\pi\hbar^3)[2m(\Phi-\mu)+(\lambda mr\sin\theta)^2]^{3/2}, \quad \text{(II.1)}$$

where

$$\Phi(\mathbf{r}) = \frac{Ze^2}{r} - e^2\int\frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}. \quad \text{(II.1a)}$$

The quantity λ is the Lagrangian multiplier on the condition of constancy of the angular momentum and has the dimensions of an angular velocity.

The quantity μ corresponds to the chemical potential and vanishes in the case of the neutral atom.

The form of the modified Thomas-Fermi equation (II.1) indicates that the model describes a rigid sphere rotating with constant angular velocity λ, and the correct value of the angular momentum is obtained by a suitable adjustment of the value of λ. This, however, is a classical treatment of the angular momentum. To begin with, the total angular momentum is taken equal to the z component in the above derivation and further, quantum mechanically it is meaningless to speak about an angular momentum for a spherically symmetric system since the wave function of such a system is invariant under rotation.[11]

This modification of the Thomas-Fermi model may be derived in an alternative fashion that is very much in the spirit of the cranking model of the nucleus. This model was first introduced by Inglis in an attempt to explain the rotational levels that arise from the more or less rigid rotation of nuclei. The derivation of the cranking model hinges on the notion that the nucleons are in a potential well that is externally rotated. We shall, therefore, rederive the Sessler-Foley modification of the Thomas-Fermi model by leaving the Fermi sphere centered at the origin in momentum space, and rotating the nuclear potential well instead.

The kinetic energy of the atom is given by

$$\frac{2}{(2\pi\hbar)^3}\int d\mathbf{r}\int d\mathbf{p}\frac{p^2}{2m} = \frac{1}{m\hbar^3}\int d\mathbf{r}\frac{p_F{}^5}{10\pi^2}. \quad \text{(II.2)}$$

[8] The problem of the statistical atom with nonzero angular momentum was recently treated by P. H. Levine and O. Von Roos, Phys. Rev. **125**, 207 (1962). Although this approach is similar to that of Baraff and Borowitz in many ways, the inclusion of angular momentum is done classically and thus their resulting equation for the density in zeroth order reduces at zero temperature to the Sessler-Foley equation.

[9] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 34.

[10] See H. Grad, Comm. on Pure and Appl. Math. **5**, 455 (1952). Also H. Grad, J. Phys. Chem. **56**, 1039 (1952). Grad has discussed the statistical mechanics of dynamical systems with integrals other than energy. In particular his approach allows him to take into account internal degrees of freedom within the individual members of the system. He does not, however, allow for the imposition of conditions derived from empirical knowledge of the internal structure of the system.

[11] See, for example, G. E. Brown, in *Lecture Notes on the Many Body Problem*, edited by C. Fronsdal (W. A. Benjamin, Inc., New York, 1962).

Rotating the nuclear potential well will have the effect of adding a centrifugal term to the potential energy which becomes

$$\int d\mathbf{r}\left\{\frac{e^2}{2}\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\frac{Ze^2}{r}+\tfrac{1}{2}mr^2\omega^2\right\}n(\mathbf{r}). \quad \text{(II.3)}$$

The energy density E' is related to the energy density E of the nonrotating system by

$$E'=E+\tfrac{1}{2}mr^2\omega^2 n(\mathbf{r}). \quad \text{(II.4)}$$

We may therefore consider the quantity

$$mr^2\bar{\omega}n(\mathbf{r}) \quad \text{(II.5)}$$

as an angular momentum density. The integral of this density over the volume of the atom is the total angular momentum which is to be conserved.

Introducing the Lagrangian multipliers λ and μ for the conditions of conservation of angular momentum and particle number, respectively, we obtain as the expression to be minimized

$$\int d\mathbf{r}\left\{\frac{\hbar^2(3\pi^2)^{5/3}}{10\pi^2 m}[n(\mathbf{r})]^{5/3}+\frac{e^2}{2}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\frac{Ze^2}{r}n(\mathbf{r})\right.$$
$$\left.+\tfrac{1}{2}mr^2\omega^2 n(\mathbf{r})+\lambda mr^2\bar{\omega}n(\mathbf{r})+\mu n(\mathbf{r})\right\}. \quad \text{(II.6)}$$

Variation with respect to $\bar{\omega}$, taking into account the fact that only components of $\bar{\omega}$ normal to the polar axis contribute to the angular momentum, yields

$$\omega=-\lambda\sin\theta. \quad \text{(II.7)}$$

Variation with respect to $n(\mathbf{r})$ in conjunction with Poisson's equation yields finally

$$\nabla^2\Phi=(4e^2/3\pi\hbar^3)[2m(\Phi-\mu)+(\lambda mr\sin\theta)^2]^{3/2},$$

which is seen to be identical with (II.1).

We see, therefore, that the external rotation of the potential well leads to the same equation for the density as that obtained from the displacement of the Fermi sphere in momentum space.

The rotational levels of nuclei so well explained by the cranking model do not appear in nuclei in the vicinity of the magic numbers. There are, for example, no rotational levels in Pb^{208} and it is only as one goes away from lead toward the heavier nuclei that rotational levels arise and the theoretical level spacing is approached. This is also true in the rare-earth region far removed from the magic numbers. We see therefore that a model based on the external rotation of a potential well has its greatest utility when applied to situations in which large numbers of particles lie outside a spherical core. We shall see that this is true in the case of the atom as well.

III. MIXED POSITION—ANGULAR MOMENTUM REPRESENTATION

We use the Green's function formalism introduced by Schwinger[12] for the quantum-mechanical many-particle system in the ground state. This description of the many-body system is a time-dependent one resembling the time-independent description of the many-body system employing the set of 1, 2, $\cdots N$ particle density matrices. In this formalism the N-particle Green's function

$$G_N(\mathbf{r}_1t_1\cdots\mathbf{r}_Nt_N;\,\mathbf{r}_1't_1'\cdots\mathbf{r}_N't_N')$$

is analogous to the N-particle density matrix and contains the same information about the system.[13] The Green's functions also satisfy a hierarchy of equations in which the N-particle Green's function is coupled to the $(N+1)$-particle and the $(N-1)$-particle Green's functions. The procedure to be adopted in what follows is that of Baraff and Borowitz in which a suitable representation of the one-particle Green's function is expanded in powers of $\hbar$.

The Hamiltonian for an atom having a nucleus of infinite mass and charge Ze at the origin surrounded by N electrons is given by

$$H=\sum_i H_0(\mathbf{r}_i)+\tfrac{1}{2}\sum_{i\neq j}v(\mathbf{r}_i-\mathbf{r}_j), \quad \text{(III.1a)}$$

$$H_0(\mathbf{r}_i)=-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Ze^2}{r_i}, \quad \text{(III.1b)}$$

$$v(\mathbf{r}_i-\mathbf{r}_j)=\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}. \quad \text{(III.1c)}$$

The first of the coupled hierarchy of integro-differential equations involving the one- and two-particle Green's functions may be written in the Hartree-Fock approximation as a pair of integral equations:

$$\int K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)d\mathbf{r}_2dt_2G_1(\mathbf{r}_2t_2;\,\mathbf{r}_1't_1')$$
$$=\hbar\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(t_1-t_1'), \quad \text{(III.2a)}$$

where the kernel $K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)$ is defined by

$$K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)$$
$$=\left[i\hbar\frac{\partial}{\partial t_1}-H_0(\mathbf{r}_1)+2i\int d\mathbf{r}'v(\mathbf{r}_1-\mathbf{r}')G_1(\mathbf{r}'t;\,\mathbf{r}'t^+)\right]$$
$$\times\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2)-iv(\mathbf{r}_1-\mathbf{r}_2)$$
$$\times G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_1^+)\delta(t_1-t_2). \quad \text{(III.2b)}$$

At this point Baraff and Borowitz effect a transformation to a mixed position-momentum representation. For

[12] J. Schwinger, Proc. Natl. Acad. Sci. U. S. **37**, 452 (1951).
[13] A. Klein and R. Prange, Phys. Rev. **112**, 994 (1958); R. Prange and A. Klein, *ibid.* **112**, 1008 (1958).

the description of an atom with nonvanishing angular momentum it will prove useful to choose a more appropriate representation. The importance of the choice of representation rests on the fact that the many-body problem we have formulated is not solved exactly. If it were, then all the properties of the system, including of course the angular momentum could be deduced from the solution independent of the representation of the Green's function. However, one is rarely so fortunate as to be dealing with a problem that is soluble exactly. If, then, as we have indicated, we wish to take the point of view that we are going to specify in our approximate solution something of the internal behavior and/or structure of the system that we may know from other sources, we must use a representation that is appropriate for the inclusion of such additional information. We introduce therefore the mixed position angular momentum representation which we have found to be most useful for these purposes.

By analogy to the Fourier transform obtained by multiplying the function to be transformed by the solution to the free-particle wave equation in Cartesian coordinates, followed by an appropriate integration, we introduce a transform that makes use of the free-particle solutions in spherical coordinates. The usefulness of this procedure is apparent when one remembers that a Fourier transform decomposes a spatial description of a particle into plane waves each corresponding to a particular linear momentum. The procedure adopted here will produce a decomposition into spherical waves each one of which carries a particular angular momentum.

The single-particle Green's function is to be transformed as follows:

$$\hat{G}_{lm}(\mathbf{R},p\omega)=\int G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)\psi_{plm}(\mathbf{r}_1)\times\exp[(i\omega/\hbar)(t_1-t_2)]d\mathbf{r}_1d(t_1-t_2)\,,\quad\text{(III.3)}$$

where

$$\psi_{plm}(\mathbf{r})=(2\pi)^{3/2}\hbar(p/\hbar r)^{1/2}J_{l+1/2}(pr/\hbar)Y_{lm}(\theta,\varphi)\,;\quad\text{(III.4)}$$

$J_{l+1/2}$ are cylindrical Bessel functions, the $Y_{lm}(\theta,\varphi)$ are normalized spherical harmonics, and

$$\mathbf{R}=\tfrac{1}{2}[\mathbf{r}_1+\mathbf{r}_2]\quad\text{(III.5)}$$

is to be held fixed in evaluating the integral defined by the transform.

The inverse transform is given by

$$G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)=\frac{1}{(2\pi\hbar)^4}\sum_{l,m}\int\hat{G}_{lm}(\mathbf{R},p\omega)\psi^*_{plm}(\mathbf{r}_1)\times\exp[-(i\omega/\hbar)(t_1-t_2)]dpd\omega\,.\quad\text{(III.6)}$$

The spatial density of the electrons may be expressed in a form that displays the usefulness of the mixed position-angular momentum representation for the atom with nonzero angular momentum,

$$n(\mathbf{R})=-iG_1(\mathbf{R}t;\,\mathbf{R}t^+)=\sum_{l,m}\int\frac{dp}{(2\pi\hbar)^3}n_{lm}(\mathbf{R},p)\psi^*_{plm}(\mathbf{R})\,,\quad\text{(III.7a)}$$

$$n_{lm}(\mathbf{R},p)=-i\int\hat{G}_{lm}(\mathbf{R},p\omega)\frac{d\omega}{2\pi\hbar}\,.\quad\text{(III.7b)}$$

Equations (III.7) suggest the following physical interpretation; the quantity $n_{lm}(\mathbf{R},p)$ is a density in a phase space that is characterized by a momentum subspace with one continuous coordinate and two discrete indices indicating the symmetry properties of the angular momentum. Physically we shall interpret $n_{lm}(\mathbf{R},p)$ as giving both the spatial distribution as well as the angular momentum distribution of electrons in the atom.

The mixed Fourier-Hankel transform of Eq. (III.2a) is taken with respect to $\mathbf{r}_1$ and t_1-t_1' keeping $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_1')/2$ constant. We obtain

$$\int K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)d\mathbf{r}_2dt_2G_1(\mathbf{r}_2t_2;\,\mathbf{r}_1't_1')\psi_{plm}(\mathbf{r}_1)\times\exp[(i\omega/\hbar)(t_1-t_1')]d\mathbf{r}_1d(t_1-t_1')=\frac{\hbar}{8}\psi_{plm}(\mathbf{R})\,.\quad\text{(III.8)}$$

The quantity $\psi_{plm}(\mathbf{r})$ may be expanded in plane waves as follows[14]:

$$\psi_{plm}(\mathbf{r})=\frac{p}{i^l}\int d\Omega_pe^{i\mathbf{p}\cdot\mathbf{r}/\hbar}Y_{lm}(\Omega_p)\,.\quad\text{(III.9)}$$

Inserting (III.8) in (III.9) and interchanging the order of integration we obtain

$$\frac{\hbar}{8}\psi_{plm}(\mathbf{R})=\frac{p}{i^l}\int d\Omega_pY_{lm}(\Omega_p)\int K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)d\mathbf{r}_2dt_2G_1(\mathbf{r}_2t_2;\,\mathbf{r}_1't_1')\times\exp\left[i\frac{\mathbf{p}\cdot\mathbf{r}_1}{\hbar}+\frac{i\omega}{\hbar}(t_1-t_1')\right]d\mathbf{r}_1d(t_1-t_1')=\frac{p}{i^l}\int d\Omega_pY_{lm}(\Omega_p)\tilde{\Gamma}\,,\quad\text{(III.10)}$$

where $\tilde{\Gamma}$ is the Fourier transform of the product of K and G defined by the above integral. This relationship between the Fourier transform $\tilde{\Gamma}_p$ and the Hankel

[14] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1467.

transform $\hat{\Gamma}_{plm}$ is quite general, i.e.,

$$\hat{\Gamma}_{plm}=\frac{p}{i^l}\int d\Omega_p Y_{lm}(\Omega_p)\tilde{\Gamma}_{\mathbf{p}}, \qquad \text{(III.11a)}$$

$$\tilde{\Gamma}_{\mathbf{p}}=\sum_{l,m}\frac{i^l}{p}Y_{lm}^*(\Omega_p)\hat{\Gamma}_{plm}. \qquad \text{(III.11b)}$$

Baraff and Borowitz have shown that the Fourier transform $\tilde{\Gamma}$ may be expanded in terms of the individual transforms $\tilde{K}$ and $\tilde{G}$ by means of a differential operator of infinite order which has the structure of an infinite series of terms each of which contains an explicit power of $\hbar$. The zeroth-order term is just the product of the individual transforms. In this approximation, therefore, (III.10) becomes

$$\begin{aligned}\frac{\hbar^{-3}}{8}\psi_{plm}(\mathbf{R})&=\frac{p}{i^l}\int d\Omega_p Y_{lm}(\Omega_p)\tilde{K}_0\tilde{G}_0\\&=\frac{p}{i^l}\int d\Omega_p Y_{lm}(\Omega_p)\tilde{K}_0\left[\sum_{\lambda,\mu}\frac{i^\lambda}{p}Y_{\lambda\mu}(\Omega_p)\hat{G}_{0\lambda\mu}\right],\end{aligned} \qquad \text{(III.12)}$$

where explicit use has been made of the expansion in powers of $\hbar$ given by Baraff and Borowitz for both the kernel as well as the one-particle Green's function. The zero subscripts on the kernel and the Green's function indicate the zeroth-order term in the expansion in $\hbar$.

At this point we would like to be able to make some statement as to the relative significance of the terms in the one-particle Green's function, in light of whatever partial knowledge we may have about the system. For this purpose we invoke certain statistical arguments. We regard the number of electrons as large and construct a microcanonical ensemble to represent the system. All possible internal distributions of angular momentum consistent with the total energy of the atom are to be regarded as equally likely. A justification of the use of the microcanonical ensemble for the isolated quantum mechanical system is discussed in detail in Tolman.[15]

If our partial knowledge of the system is such that we know that the angular momentum of the system is carried by a single particle, then it is clear that this can occur in only one way and as we shall see, there is an unambiguous form of the one-particle Green's function that describes this situation. On the other hand, if we know the angular momentum of the system is carried by many particles, the situation is not as clear. This is because there are many possible internal distributions of angular momentum that will give rise to the same total angular momentum. We are, however, dealing with an equilibrium state of the atom since we are describing the ground state; and therefore, we shall adopt the procedure of choosing the most probable configuration to represent the system.

Let us therefore begin by asking what is the most probable configuration resulting from the addition of many angular momenta, corresponding to the situation in which many electrons contribute to the total angular momentum.

Consider the N_l electrons each carrying an angular momentum l. The resultant angular momentum of these electrons lies between zero and lN_l. If we consider each possible arrangement of these electrons equally probable, then the resultant angular momentum is shown in an Appendix to be a random variable that obeys the central limit theorem. The distribution of the resultant angular momentum tends, therefore, toward a Gaussian distribution centered at zero angular momentum. This, however, is true for all l and since the distribution of a finite number of random variables each of which has a Gaussian distribution is itself Gaussian, we have the result that the distribution of resultant angular momentum is peaked at zero angular momentum.

In order to estimate how the sharpness of the distribution depends on the number of electrons we note that the various possible vector additions of individual angular momenta are equivalent to the various possible trajectories in a random-walk problem. The probability distribution of the sum L of a large number N of individual random steps of mean square size $\langle l^2\rangle_{\text{av}}$ [16] is

$$W(L)=\frac{\exp\{-L^2/2N\langle l^2\rangle_{\text{av}}\}}{[2N\langle l^2\rangle_{\text{av}}]^{3/2}}. \qquad \text{(III.13)}$$

The variance of the distribution is

$$\sigma=[N\langle l^2\rangle_{\text{av}}]^{1/2}, \qquad \text{(III.14)}$$

while the maximum possible angular momentum is

$$L_{\max}=N[\langle l^2\rangle_{\text{av}}]^{1/2}. \qquad \text{(III.15)}$$

We see therefore that the distribution of the resultant angular momentum becomes more sharply peaked about the origin, i.e., zero angular momentum with increasing number of particles since

$$\sigma/L_{\max}=N^{-1/2}. \qquad \text{(III.16)}$$

We therefore, in attempting to describe the situation in which many electrons contribute to the angular momentum consider only the spherically symmetric term in (III.6) and in the sum on the right-hand side of (III.12) corresponding to the most probable single configuration of the system.

[15] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Chap. 9.

[16] See, for example, S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

In that case (III.12) becomes

$$\frac{\hbar^{-3}}{8}\psi_{plm}(\mathbf{R})=\frac{\hat{G}_{000}}{4\pi}\cdot\frac{1}{i^l}\int d\Omega_p Y_{lm}(\Omega_p)\tilde{K}_0 = \frac{\hat{G}_{000}\hat{K}_{0lm}}{4\pi p}, \quad \text{(III.17)}$$

where

$$\hat{K}_{0lm}(\mathbf{R},p\omega) = \left\{\omega-\frac{p_r^2}{2m}-\frac{l(l+1)\hbar^2}{2mR^2}-2\int v(\mathbf{R}-\mathbf{r})n_{000}(\mathbf{r})d\mathbf{r}\right\}\frac{\psi_{plm}(\mathbf{R})}{8}$$

$$\equiv\{\omega-E(\mathbf{R},pl)\}\frac{\psi_{plm}(\mathbf{R})}{8}. \quad \text{(III.18)}$$

The zeroth-order density $n_{000}(\mathbf{R},p)$ is related to $\hat{G}_{000}(\mathbf{R},p\omega)$ by

$$n_{000}(\mathbf{R},p)=-i\int\frac{d\omega}{2\pi}e^{i\omega 0+}\hat{G}_{000}(\mathbf{R},p\omega) \quad \text{(III.19a)}$$

and

$$n_{000}(\mathbf{R})=\int\frac{dp}{(2\pi)^3}n_{000}(\mathbf{R},p)\psi^*_{p00}(\mathbf{R}). \quad \text{(III.19b)}$$

We have therefore,

$$\hat{G}_{000}(\mathbf{R},p\omega)=\frac{\hbar^{-3}4\pi p}{\omega-E(\mathbf{R},pl)} \quad \text{(III.20)}$$

to be integrated in the complex ω plane. For the case at hand, i.e., an atom in its ground state the path of integration lies just below the real ω axis from $-\infty<\omega<\mu$, crosses the axis at μ and lies just above the real axis from $\mu<\omega<\infty$. The constant μ is the chemical potential. The contour is completed by the upper semicircle at infinity. The derivation of the contour is discussed fully in an appendix to the Baraff and Borowitz paper.

The result of the integration in the ω plane is

$$n_{000}(\mathbf{R},p)=4\pi p\hbar^{-3}, \quad E(\mathbf{R},pl)<\mu, \qquad =0, \quad E(\mathbf{R},pl)>\mu. \quad \text{(III.21)}$$

The spatial density may be obtained from $n_{000}(\mathbf{R},p)$ by means of Eq. (III.19b) which yields

$$n_{000}(\mathbf{R})=\frac{1}{6\pi^2\hbar^3}\left[2m(\mu-\Phi)-\frac{l(l+1)\hbar^2}{R^2}\right]^{3/2}, \quad \text{(III.22)}$$

where

$$\Phi(\mathbf{R})=\frac{-Ze^2}{R}+2\int v(\mathbf{R}-\mathbf{r})n_{000}(\mathbf{r})d\mathbf{r}. \quad \text{(III.23)}$$

Equation (III.22) in conjunction with Poisson's equation has the structure of the Sessler-Foley modification of the Thomas-Fermi model. This is due to the appearance of the centrifugal potential on the right-hand side. One may, however, ask why such a term appears since the Green's function used in the derivation was taken to be spherically symmetric. It is present because of the angular dependence of the transform of the kernel. The question remains however, as to what value of l is to be used in (III.22). To bring the model into coincidence with the Sessler-Foley model we shall choose l such that

$$J(J+1)\hbar^2=\int l(l+1)\hbar^2 n_{000}(\mathbf{R})d\mathbf{R},$$

where $J(J+1)\hbar^2$ is the square of the angular momentum of the atom. Thus l has the significance of an average angular momentum per particle.

As pointed out by Sessler and Foley, this model corresponds to a spherical electron density executing a rigid rotation. The model does not yield any of the characteristic properties of the periodic table and the essentially classical fashion in which the angular momentum appears is exhibited by the vanishing of the quantum mechanical expectation value of the angular momentum.

In the Hartree-Fock approximation the quantum mechanical expectation value of the square of angular momentum is given by

$$-i\int\lim_{1'\to 1}L^2(1)G(11')d(1)+\frac{(-i)^2}{2!}\int\lim_{1'\to 1,2'\to 2}2\mathbf{L}(1)\cdot\mathbf{L}(2) \times[G(11')G(22')-G(12')G(21')]d(1)d(2), \quad \text{(III.24)}$$

which may be evaluated by the insertion of the form of the one-particle Green's function employed in our derivation of the Sessler-Foley result, i.e.,

$$G_1(\mathbf{r}_1t_1;\mathbf{r}_2t_2)=\frac{1}{(2\pi\hbar)^4}\int\hat{G}_{00}(\mathbf{R},p\omega)\psi^*_{p00}(\mathbf{r}_1) \times\exp\left[-\frac{i\omega}{\hbar}(t_1-t_2)\right]dpd\omega. \quad \text{(III.25)}$$

If (III.25) is inserted in (III.24) and the center-of-mass coordinate R regarded as a parameter, the expectation value of the square of the angular momentum is found to vanish because of the zero eigenvalue of the angular part of $\psi_{p00}(\mathbf{r}_1)$.

We see, therefore, that if nothing is known about the internal distribution of the angular momentum we are led to the Sessler-Foley result as was to be expected on the basis of the Landau and Lifshitz theorem quoted above. We are, however, in possession of a great deal of qualitative information about the internal distribution of angular momentum in an atom. We would, therefore, be led to expect that if we could include some of this information we would be led to a better model. In the context of the present formalism, this amounts to choosing a more appropriate approximation than $\hat{G}_{00}(\mathbf{R},p\omega)$ for the Fourier-Hankel transform of the one-particle Green's function.

There is a relatively simple form of the one-particle Green's function that corresponds physically to the case of one, two, or three electrons outside a closed shell and has the virtue of yielding the proper expectation value of the angular momentum. A trivial modification of the form of this Green's function will be seen to correspond physically to electrons missing from a closed shell.

The one-particle Green's function is taken to be of the form

$$G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)=G_1^0(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)+G_1^L(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)\,,\quad\text{(III.26a)}$$

where G_1^0 will be seen to describe the behavior of the core and G_1^L that of the valence electrons. The Hankel decomposition of the Green's function is given by

$$G_1^0(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)=\frac{1}{(2\pi\hbar)^4}\int\hat{G}_{00}(\mathbf{R},p\omega)\psi^*_{p00}(\mathbf{r}_1)\times\exp\left[-\frac{i\omega}{\hbar}(t_1-t_2)\right]dpd\omega\quad\text{(III.26b)}$$

and

$$G_1^L(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)=\frac{1}{(2\pi\hbar)^4}\int\hat{G}_{Lm}(\mathbf{R},p\omega)\psi^*_{pLm}(\mathbf{r}_1)\times\exp\left[-\frac{i\omega}{\hbar}(t_1-t_2)\right]dpd\omega\,.\quad\text{(III.26c)}$$

Since the normalization on the one-particle Green's function is

$$-i\int G_1(\mathbf{r}_1t_1;\,\mathbf{r}_1t_1^+)d\mathbf{r}_1=N\,,\quad\text{(III.27a)}$$

a suitable normalization on the quantities just introduced is given by

$$-i\int G_1^0(\mathbf{r}_1t_1;\,\mathbf{r}_1t_1^+)d\mathbf{r}_1=N-n\,,\quad\text{(III.27b)}$$

$$-i\int G_1^L(\mathbf{r}_1t_1;\,\mathbf{r}_1t_1^+)d\mathbf{r}_1=n\,.\quad n=0,\,1,\,2,\,3\,.\quad\text{(III.27c)}$$

We likewise assume that the two-particle Green's function may be decomposed into

$$G_2(11';\,22')=G_2^0(11';\,22')+G_2^L(11';\,22')\,,\quad\text{(III.28a)}$$

where

$$G_2^0(11';\,22')=\frac{1}{(2\pi\hbar)^8}\int G_2(\mathbf{R},p00\omega;\,\mathbf{R}',p'00\omega')\psi^*_{p00}(\mathbf{r}_1)\psi^*_{p'00}(\mathbf{r}_2)\times\exp\left[-\frac{i\omega}{\hbar}(t_1-t_1')-\frac{i\omega'}{\hbar}(t_2-t_2')\right]\times dpdp'd\omega d\omega'\quad\text{(III.28b)}$$

and

$$G_2^L(11';\,22')=\frac{1}{(2\pi\hbar)^8}\sum_{m,m'}C_{LL}(LM,mm')\times\int G_2(\mathbf{R},pLm\omega;\,\mathbf{R}',p'Lm'\omega')\psi^*_{pLm}(\mathbf{r}_1)\psi^*_{p'Lm'}(\mathbf{r}_2)\times\exp\left[-\frac{i\omega}{\hbar}(t_1-t_1')-\frac{i\omega'}{\hbar}(t_2-t_2')\right]\times dpdp'd\omega d\omega'\,.\quad\text{(III.28c)}$$

The C_{LL} appearing in (III.28) are Clebsch-Gordan coefficients.[17]

In choosing appropriate normalizations for the two terms in (III.28a), we observe that the normalization of the two-particle Green's function should be

$$\frac{(-i)^2}{2}\int G_2(11^+;\,22^+)d(1)d(2)=\tfrac{1}{2}N(N-1)\,,\quad\text{(III.29)}$$

corresponding to the number of distinct pairs that one may choose from N objects. We shall therefore choose the normalization of the two terms in the two-particle Green's function as follows:

$$\frac{(-i)^2}{2}\int G_2^0(11^+;\,22^+)d(1)d(2)=\tfrac{1}{2}(N-n)(N-n-1)\quad\text{(III.30a)}$$

and

$$\frac{(-i)^2}{2}\int G_2^L(11^+;\,22^+)d(1)d(2)=\tfrac{1}{2}n(n-1)\,.\quad\text{(III.30b)}$$

This normalization corresponds to the separate antisymmetrization of the core and the contents of the outer shell. The coupling of the core and valence electrons via the kernel K is, however, kept intact.

If we apply (III.24) to the forms of the one- and two-particle Green's functions chosen here, we obtain

$$-i\int\lim_{1'\to1}L^2(1)[G_1^0(11')+G_1^L(11')]d(1)+\frac{(-i)^2}{2}\int\lim_{1'\to1,2'\to2}2\mathbf{L}(1)\cdot\mathbf{L}(2)\times[G_2^0(11';\,22')+G_2^L(11';\,22')]d(1)d(2)\,.\quad\text{(III.31)}$$

[17] This choice for the two-particle Green's function can be understood more readily by considering the two-particle Green's function in a momentum representation. It is then seen that the form chosen here corresponds for suitable time ordering to the addition and subsequent removal of two particles each carrying a particular angular momentum, subject to the restriction that the angular momentum of the pair of particles is well defined.

Substituting (III.26) and (III.28) in (III.31) and remembering that

$$L^2-L_1^2-L_2^2=2\mathbf{L}_1\cdot\mathbf{L}_2,$$

we obtain

$$L(L+1)\hbar^2[n-\tfrac{1}{2}n(n-1)]. \qquad \text{(III.32)}$$

We thus obtain a zero angular momentum for the case of no electrons outside a spherical core and $L(L+1)\hbar^2$ for the square of the total angular momentum in the case of either one or two electrons outside a spherical core. In the case of three electrons outside a core, the angular momentum is seen to vanish corresponding to the fact that the elements of the principal groups in the fifth column of the periodic table have three p electrons outside a spherical core which combine to give an S state for the ground state.

Having found a form for the Green's functions that describes one, two, or three electrons outside a closed shell and that yields the proper quantum mechanical expectation value of the angular momentum we proceed as before to obtain an equation for the electron density. Equation (III.12) becomes

$$\frac{p}{i^L}\int d\Omega_p Y_{Lm}(\Omega_p)\tilde{K}_0[\tilde{G}_0{}^0+\tilde{G}_0{}^L]=\frac{\hbar^{-3}}{8}\psi_{pLm}(\mathbf{R}). \qquad \text{(III.33)}$$

In this case the L appearing in the Fourier-Hankel transform is taken to be the same as that of the term G_0. As before, we may evaluate the first integral, obtaining

$$\frac{\hat{K}_{0Lm}\hat{G}^0_{000}}{4\pi p}=\frac{[\omega-E(\mathbf{R},pL)]}{4\pi p}\times\frac{\psi_{pLm}(\mathbf{R})}{8}\hat{G}^0_{000}(\mathbf{R},p\omega). \qquad \text{(III.34)}$$

In order to evaluate the second integral, we note the relationship between the Fourier transform and the Hankel transform,

$$\tilde{G}_0{}^L(\mathbf{R},p\omega)=\sum_{\lambda\mu}\frac{i^\lambda}{p}Y^*_{\lambda\mu}(\Omega_p)\hat{G}^L_{0\lambda\mu}(\mathbf{R},p\omega)$$
$$=\frac{i^L}{p}Y^*_{Lm}(\Omega_p)\hat{G}^L_{0Lm}(\mathbf{R},p\omega), \qquad \text{(III.11b)}$$

where the last step was obtained using the explicit form of $G_1{}^L$. Using the expansion of a product of spherical harmonics,

$$Y_{lm}(\Omega_p)Y^*_{lm}(\Omega_p)$$
$$=\sum_{\lambda\mu}\frac{(-)^m(2l+1)}{[4\pi(2l+1)]^{1/2}}C_{ll}(\lambda,000)C_{ll}(\lambda\mu,m,-m)Y_{\lambda\mu}(\Omega_p)$$
$$\equiv\sum_{\lambda\mu}B_{Lm}{}^{\lambda\mu}Y_{\lambda\mu}(\Omega_p), \qquad \text{(III.35)}$$

where the C_{ll} are the usual Clebsch-Gordan coefficients, and inserting (III.11b), (III.35) in (III.33) yields for the second integral in the latter equation

$$\frac{p}{i^L}\int d\Omega_p Y_{Lm}(\Omega_p)\tilde{K}_0\tilde{G}_0{}^L$$
$$=\hat{G}_{0Lm}\cdot\frac{i^L}{p}\sum_{\lambda\mu}B_{Lm}{}^{\lambda\mu}\frac{\psi_{p\lambda\mu}(\mathbf{R})}{8}[\omega-\bar{E}], \qquad \text{(III.36a)}$$

where

$$\bar{E}=\frac{\sum_{\lambda\mu}E(\mathbf{R},p\lambda)B_{Lm}{}^{\lambda\mu}\psi_{p\lambda\mu}(\mathbf{R})}{\sum_{\lambda\mu}B_{Lm}{}^{\lambda\mu}\psi_{p\lambda\mu}(\mathbf{R})}. \qquad \text{(III.36b)}$$

Thus Eq. (III.33) becomes

$$\frac{\hat{G}^0_{000}(\mathbf{R},p\omega)}{4\pi|p|}+\frac{\hat{G}^L_{0Lm}(\mathbf{R},p\omega)}{|p|}\cdot\frac{i^L\sum_{\lambda\mu}B_{Lm}{}^{\lambda\mu}\psi_{p\lambda\mu}(\mathbf{R})}{\psi_{pLm}(\mathbf{R})}$$
$$\times\left[\frac{\omega-\bar{E}}{\omega-E(\mathbf{R},pL)}\right]=\frac{\hbar^{-3}}{\omega-E(\mathbf{R},pL)}. \qquad \text{(III.37)}$$

Since $\hat{G}^0_{000}$ is of the order of N times larger than $\hat{G}^L_{0Lm}$, we may solve first for the core density in the absence of the outer electrons obtaining as in (III.20) (the Sessler-Foley model)

$$\hat{G}_{000}{}^0(\mathbf{R},p\omega)=\frac{\hbar^{-3}4\pi p}{\omega-E(\mathbf{R},pL)}. \qquad \text{(III.38)}$$

Since the functional variation of $\hat{G}^0_{000}(\mathbf{R},p\omega)$ for $N-n$ particles is the same as for the N in the Sessler-Foley model, we may write (III.37) as

$$\hat{G}_{0Lm}(\mathbf{R},p\omega)\frac{i^L\sum_{\lambda\mu}B^{\lambda\mu}_{Lm}\psi_{p\lambda\mu}(\mathbf{R})}{\psi_{pLm}(\mathbf{R})}=\frac{n\hbar^{-3}}{N[\omega-\bar{E}]} \qquad \text{(III.39a)}$$

and

$$\hat{G}_{000}(\mathbf{R},p\omega)=\left(\frac{N-n}{N}\right)\frac{4\pi p\hbar^{-3}}{\omega-E(\mathbf{R},pL)}. \qquad \text{(III.39b)}$$

Integrating as before over the complex energy plane, we obtain

$$n_{0Lm}(\mathbf{R},p)=4\pi p\hbar^{-3}\cdot\left(\frac{n}{N}\right)\frac{\psi_{pLm}(\mathbf{R})}{4\pi i^L\sum_{\lambda\mu}B^{\lambda\mu}_{Lm}\psi_{p\lambda\mu}(\mathbf{R})};$$
$$\bar{E}<\mu, \qquad \text{(III.40a)}$$

$$n_{000}(\mathbf{R},p)=4\pi p\hbar^{-3}\left(\frac{N-n}{N}\right);\quad E(\mathbf{R},pL)<\mu. \qquad \text{(III.40b)}$$

The spatial density for the core is obtained by integrating over momentum, yielding

$$n_{000}(\mathbf{R})=\left(\frac{N-n}{N}\right)\frac{1}{6\pi^2\hbar^3}\times\left\{2m(\mu-\Phi)-\frac{L(L+1)\hbar^2}{R^2}\right\}^{3/2} \quad \text{(III.41)}$$

to the same order that yielded (III.22).

We may obtain a spatial density from (III.40a) that corresponds to what one might expect on physical grounds by approximating the series in the denominator by the first term. In that case

$$n_{0Lm}(\mathbf{R})=\left(\frac{n}{N}\right)\times\frac{R^{2L}Y^2_{Lm}[2m(\mu-\Phi)-L(L+1)\hbar^2/R^2]^{(2L+3)/2}}{2\pi^2(2L+3)\hbar^{2L+3}}. \quad \text{(III.42)}$$

It is seen that in the case of vanishing angular momentum the present case reduces to the Thomas-Fermi model.

In the event that the atom may be approximately described by one, two, or three electrons outside a closed core carrying the entire angular momentum, we have seen that it is possible to construct a form for the one-particle Green's function that in the Hartree-Fock approximation leads to the proper quantum mechanical expectation value of the angular momentum. The equations for the spatial electron density that are recovered from this form for the Green's function differ from those obtained by Sessler and Foley.

We may treat the cases of one, two, or three electrons missing from a closed shell by slightly modifying our previous procedure. We let $n\rightarrow -n$ in (III.27) and (III.30), thereby obtaining for the expectation value of the angular momentum in (III.32)

$$L(L+1)\hbar^2[-n-\tfrac{1}{2}n(n+1)]. \quad \text{(III.43)}$$

Then once again for no electron missing from a spherical core we obtain a vanishing angular momentum. For the case of either one or two electrons missing from a spherical core we obtain the proper angular momentum with $n=-1$ and $n=-2$, respectively. In the case of three electrons missing from a closed core we return once again to column five of the periodic table with a ground S state.

IV. QUADRUPOLE COUPLING CONSTANT

The present model has been derived not in an attempt to calculate very accurate detailed atomic properties but rather to illustrate that a statistical model including available information about the internal behavior of the system will yield better results. We have therefore chosen to compare a calculation based on the present model with a similar one done by Sessler and Foley.

The quantity to be calculated is the quadrupole coupling constant

$$q=-\int\frac{3\cos^2\theta-1}{R^3}n(\mathbf{R})d\mathbf{R}. \quad \text{(IV.1)}$$

In the case of the halogens, we may consider the core density to a first approximation to be spherically symmetric, the only contribution to the quadrupole coupling constant coming from the missing electron. Since the sign of the second term in (III.26a) will differ in the case of a single electron missing from a closed shell as compared to a single valence electron, we see that this model is capable of accounting for a sign change in the quadrupole coupling constant at a closed shell whereas the Sessler-Foley model was not.

Neglecting the centrifugal potential in (III.42) we obtain for the case of the halogens

$$q=\frac{\langle 3\cos^2\theta-1\rangle_{p_{3/2}}}{2\pi^2\hbar^{2L+3}(2L+3)Z}\times\int_{R\min}^{\infty}R^{2L-1}[2m\Phi]^{(2L+3)/2}dR. \quad \text{(IV.2)}$$

The form of the Thomas-Fermi potential is such that the integral diverges at the lower limit and must be cut off at some appropriate point. In order to arrive at a reasonable lower limit for the integration we note that the lower limit of the validity of the Thomas-Fermi model is a_0/Z,[18] which is the radius of the first Bohr orbit in the field of a nucleus of charge Ze. That very little should be lost by cutting off the integral at this point can be seen by considering what fraction of the charge of an electron in the lowest p state in hydrogen lies within a sphere of radius a_0. The charge inside a sphere of radius a_0 in this case is approximately $0.004e$ which is larger than the amount of charge found within the first Bohr orbit for higher p states and for higher angular momentum states as well. In addition, for higher Z this fraction decreases as Z^5.

Using a_0/Z as a lower limit, we obtain for the quadrupole coupling constants of the halogens

$$q_{\mathrm{Cl}}a_0^3=-2.4,$$
$$q_{\mathrm{Br}}a_0^3=-21,$$
$$q_{\mathrm{I}}a_0^3=-51.$$

These figures are within an order of magnitude of the

[18] See, for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics–Non-Relativistic Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 238.

accepted values[19] and the magnitudes increase with increasing Z, as opposed to the Sessler-Foley model where q varies as $Z^{-2/3}$ for all values of the angular momentum.

The primary difficulty in calculating the quadrupole coupling constant in any kind of a Thomas-Fermi model is that the density is related to the self-consistent potential and not to the square of a one-electron wave function. In the vicinity of the origin the square of the one-electron wave function in all but S states is small, in contrast to the self-consistent potential which becomes increasingly Coulombic in character as one approaches the origin. However, it is precisely this region near the origin that is weighted most heavily by the quadrupole coupling constant.

V. CONCLUSION

We have shown that a formalism that allows for the insertion of empirical information about the internal distribution of angular momentum yields a better statistical atom than that which would be obtained by requiring only that the system have an angular momentum. Thus, this model might well serve to yield a starting self-consistent potential in a machine Hartree-Fock calculation. Moreover it is also anticipated that the approach used in the present paper may be fruitfully utilized in a "Thomas-Fermi"-like model of the nucleus.

Of greater importance, perhaps, is the fact that the notions of the present work may be used in the treatment of any bound fermion system. Thus, empirical information of any form about the system may be inserted into the formalism by imposing restrictions on an appropriate representation of the Green's functions.

APPENDIX: THE CENTRAL LIMIT THEOREM AS APPLIED TO THE ADDITION OF MANY ANGULAR MOMENTA

The various possible values of the resultant angular momentum of N_l electrons each carrying an angular momentum l are given by the absolute value of the algebraic sum of N_l terms each of which may take on the $2l+1$ integral values between l and $-l$. In order to determine the distribution of the resultant angular momentum we make use of the central limit theorem which states that the sum of n random variables of mean zero tends to a Gaussian distribution provided

(a) the random variables possess absolute moments of order $2+\delta>2$

and

(b) the quotient

$$\omega_n=\sum_{i=1}^{n}\mu_{2+\delta}{}^{(i)}/B_n{}^{1+\delta/2}\underset{n\to\infty}{\longrightarrow}0,$$

where $\mu_{2+\delta}{}^{(i)}$ is the $(2+\delta)$th moment of the ith variable and B_n is the mean square fluctuation of the sum of the first n variables, i.e., the mean square fluctuation of the quantity $\sum_{i=1}{}^{n} k_i$.

For a fixed l the distribution function is

$$f(k)=\frac{1}{2l+1}\sum_{m=-l}^{l}\delta_{mk}.$$

The third absolute moment exists since

$$\mu_3=\sum_k|k^3|f(k)=\frac{1}{2l+1}\sum_{m=-l}^{l}|m^3|=\frac{2}{2l+1}\left[\frac{l(l+1)}{2}\right]^2.$$

The mean square fluctuation of k_i is

$$\langle\Delta k_i{}^2\rangle_{\mathrm{av}}=\langle k_i{}^2\rangle_{\mathrm{av}}-\langle k_i\rangle_{\mathrm{av}}{}^2,$$

$$\langle k_i\rangle_{\mathrm{av}}=\sum_k k_i f(k_i)=\sum_{m=-l}^{l}\frac{m}{2l+1}=0,$$

$$\langle k_i{}^2\rangle_{\mathrm{av}}=\sum_k k_i{}^2 f(k_i)=\sum_{m=-l}^{l}\frac{m^2}{2l+1}=\tfrac{1}{3}l(l+1).$$

Thus $\langle\Delta k_i{}^2\rangle_{\mathrm{av}}=\frac{1}{3}l(l+1)$ and $B_n=n\langle\Delta k_i{}^2\rangle_{\mathrm{av}}=\frac{1}{3}nl(l+1)$. The quotient ω_n therefore becomes

$$\omega_n=\frac{2}{2l+1}\frac{[l(l+1)/2]^2}{[l(l+1)/3]^{3/2}}\left(\frac{n}{n^{3/2}}\right),$$

which goes to zero as $n^{-1/2}$ with increasing n.

Since the distribution of angular momentum satisfies the central limit theorem, it tends in the limit of large n to a Gaussian distribution, which was to be shown.

[19] N. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956); R. B. Leighton, *Principles of Modern Physics* (McGraw-Hill Book Company, Inc., New York, 1959).