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A MODEL FOR THE STATISTICAL ATOM WITH NON-VANISHING ANGULAR MOMENTUM

Judah L. Schwartz and Sidney Borowitz

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DECEMBER 1962

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ABSTRACT

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 h 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.

ERRATA

Page 8 Eq. II.8 $J\hbar = \int (\underline{r}\times\underline{D}(\underline{r}))n(\underline{r})d\underline{r}$

13 Line 8 Read $G_N(\underline{r}_1 t_1 \ldots \underline{r}_N t_N; \underline{r}_1' t_1 \ldots \underline{r}_N' t_N)$

16 Eq. III.7 Read $\Psi_{p\ell m}(\underline{r}) = (2\pi)^{3/2}\hbar\sqrt{p/\hbar r}\, J_{\ell+1/2}(pr/\hbar)Y_{\ell m}(\theta,\phi)$

17 Eq. III.14 Read for right hand side $(2\pi\hbar)^4 G_1(\underline{r}_1' t_1' \underline{r}_2' t_2')$

19 The second line of Eq. III.19 should read

$|p|/i^{\ell}\iint\ldots\exp i/\hbar(\underline{p}\cdot\underline{r}_1 + \omega(t_1-t_1'))\, d\underline{r}_1 d(t_1-t_1')$

Eq. III.20 Read $KG_{\underline{p}}$ instead of KG_p

N.B. The quantity p refers to the magnitude of the momentum unless otherwise indicated. The argument of the spherical harmonic is $(\Omega_{\underline{p}})$.

21 Line 11 Read ....This, however, is true for all ℓ and ...

Eq. III.22 For ℓ^2 read $\overline{\ell^2}$.

22 Eq. III.24 $L_{max} = N(\overline{\ell^2})^{1/2}$

Eq. III.26 Read $\hat{G}_{ooo}$ instead of G_{ooo}.

Eq. III.27 Read $\hbar^2$ instead of t^2 .

24 Line 14 Read ....Thus ℓ has the significance ....

25 Eq. III.33 The operator in the second integral should be $2L(1)\cdot L(2)$.

28 Line 16 Read ... table have three p electrons...

30 Eq. III.45a The denominator should read $\sum_{\lambda\mu} B_{Lm}^{\lambda\mu}\Psi_{p\lambda\mu}(\underline{R})$.

Eq. III.49a The right hand side should read

$$\frac{4\pi p\hbar^{-3}n}{N}\cdot\frac{\Psi_{pLm}(\underline{R})}{4\pi i^{L}\sum_{\lambda\mu}B_{Lm}^{\lambda\mu}\Psi_{p\lambda\mu}(\underline{R})}$$

I. INTRODUCTION

The method of Thomas[1] and Fermi[2] allows one to calculate a charge distribution for an atom having no net angular momentum. This is usually done by assuming that the electrons in the atom constitute a degenerate Fermi gas at zero temperature, thereby allowing one to obtain a relationship between the Fermi momentum and the spatial density. The potential energy is expressed in terms of the electron density and finally the total energy is varied subject to the condition that the number of electrons be fixed. The result of this variation in conjunction with Poisson's equation yields a second order non-linear differential equation for the self-consistent potential in the atom. The electron density may then be recovered from the solution for the potential.

The Thomas-Fermi equation as ordinarily derived describes an atom with vanishing angular momentum since the assumed a priori density in phase space is spherically symmetric. Sessler and Foley[3] have extended the Thomas-Fermi model to include non-vanishing angular momentum in the hope of obtaining a model that would include angular "correlations". This was done in order to deal with certain atomic properties that are particularly sensitive to the angular distribution of electrons in the atom, in particular the quadrupole coupling constant.

In order to insert an angular momentum into the statistical atom Sessler and Foley introduce a departure from spherical symmetry in phase space by displacing the Fermi sphere from the origin by a position dependent amount.

There is, therefore, a net linear momentum at each point in the atom and an angular momentum may now be introduced in what is essentially a classical fashion. Once again the energy of the atom is expressed in terms of the electron density, and the total energy is varied subject to the constraints that both the number of electrons and the angular momentum be constant.

In Section II we shall show that the Sessler-Foley modification of the Thomas-Fermi model may be derived in an alternative fashion, i.e. by rotating the nuclear potential while leaving the Fermi sphere centered at the origin in momentum space. However, this is precisely the way in which the "cranking model" of the nucleus first introduced by Inglis[4-5] to explain low lying nuclear rotational levels is constructed. Indeed, many of the features of the cranking model have direct analogues in the Sessler-Foley modification of the Thomas-Fermi model. The correct value of the angular momentum is obtained through a suitable adjustment of the angular velocity of the potential. This procedure, however, does not allow for a proper description of the symmetries of the spatial charge distribution that are associated with a quantum mechanical angular momentum. The model, therefore, is not able to yield any of the properties of the atom that vary in the characteristic way of the periodic table. The quadrupole coupling constant, for example, as calculated by Sessler and Foley is always of the same sign and has the same z dependence independent of the value of the angular momentum.

In treating a quantum mechanical system statistically, one sets up

an ensemble of systems the average properties of which are taken to be reasonable estimates of the behavior of the actual system of interest. The representative ensemble is chosen so as to agree with our partial knowledge of the system of interest and is otherwise constructed in accordance with some postulate as to the a priori likelihood of different possibilities.

In the case of the statistical atom the partial information used in the Sessler and Foley work consists of a knowledge of the energy and the total angular momentum. All possible states consistent with the energy and angular momentum of the system are assumed equally probable. However, one has available a fair amount of qualitative information as to the internal distribution of angular momentum in the atom which could be used to restrict further the volume in phase space available to the system. In fact for the elements in the principal groups the angular momentum is known to be carried by either one, two or three electrons either added to or missing from a spherical core.

We have, therefore, addressed ourselves once again to the problem of attaining an approximate description of the atom that preserves in addition to the energy some other quantum number, in particular the value of the total angular momentum. In order to go beyond the work of Sessler and Foley we shall make use of the fact that we are not in total ignorance as to how the angular momentum is distributed within the atom. Including this information enables us to obtain atomic properties that vary in the characteristic fashion of the periodic table.

We shall also show, within the context of the present formalism, that in the limit of no knowledge of the internal distribution of angular momentum the Sessler-Foley result remains as the only thing one can say about the statistical atom with angular momentum.

The present work utilizes the approach of Baraff and Borowitz[6] in applying the Green's function techniques of the many body problem to the atom. In their work a mixed position momentum representation of the one particle Green's function was expanded in powers of $\hbar$. The lowest order term is seen to lead to the Thomas-Fermi density and higher order terms yield both the exchange and quantum corrections to the density. One of the attractive features of the method is that no a priori assumptions are made about the nature of the density in phase space.

In order to construct a formalism within the framework of which we may derive a modified Thomas-Fermi model with non-vanishing angular momentum we shall introduce in Section III a mixed position-angular momentum representation of the one particle Green's function. This is accomplished through the use of a mixed Fourier-Hankel transform. The transform and its inverse are defined and the physical significance of the transform is discussed.

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. One then attempts to identify those terms that are significant in any given physical situation. In the

event that the angular momentum of the atom is due to one, two or three electrons outside a spherically symmetric shell a form for the one particle Green's function is obtained that yields the proper quantum mechanical expectation value of the angular momentum. A modification of this form allows one to discuss the case of one, two or three electrons missing from a closed shell. In the Hartree-Fock approximation the first of the coupled integro-differential equations satisfied by the Green's functions is solved to lowest order in $\hbar$ and a modified Thomas-Fermi model is obtained.

On the other hand, if many electrons contribute to the angular momentum it is shown that a different assumption about the form of the one particle Green's function in the mixed position-angular momentum representation must be made. The resulting equation for the electron density in the atom in this case turns out to be the Sessler-Foley modification of the Thomas-Fermi model. The quantum mechanical expectation value of the angular momentum vanishes in this case. This is to be expected since the Sessler-Foley model corresponds to the uniform rotation of a rigid sphere.[7]

In Section IV the present model is used to investigate the behavior of the quadrupole coupling constant. The sign of the constant is shown to be given correctly and the value of the constant is shown to increase with z in the case of the halogens. The calculated values are within an order of magnitude of the accepted values.

II THE SESSLER-FOLEY AND CRANKING MODELS

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[8] 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 can be shown in the following fashion:

Let the system be subdivided into small parts. Each part is to be sufficiently large, however, that an entropy function may be defined for it. Let m_i, P_i and E_i denote the mass, momentum and energy of the ith part of the system, respectively. The entropy of the system is then

II. 1 $$S = \sum_i S_i\left(E_i - \frac{P_i^2}{2m_i}\right)$$

In addition, for a closed system we have,

II. 2a $$\sum_i \overline{P}_i = \text{CONSTANT}$$

II. 2b $$\sum_i \overline{r}_i \times \overline{P}_i = \text{CONSTANT}$$

We now introduce the Lagrangian multipliers $\overline{a}$ and $\overline{b}$ and maximize the entropy subject to the constraints that the momentum and angular momentum of the system be conserved.

The variation yields the result that for maximum entropy

II. 3 $$\frac{\overline{p}_i}{m_i} = \overline{a}T - (\overline{r}_i \times \overline{b}T)$$

where T is the temperature. We see, therefore, that the only macroscopic motions consistent with a statistical system in equilibrium are linear translation with velocity $\overline{a}T$ and uniform rotation with angular velocity $\overline{b}T$.

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 for different results than those illustrated above.[8a]

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 $\overline{D}(\underline{r})$. This imparts a net linear

momentum to each point in the atom and a non-zero angular momentum is now possible. The calculation is outlined briefly.

The kinetic energy is given by

II. 4 $$E_k = \frac{2}{(2\pi\hbar)^3}\int d\underline{r}\int d\underline{p}\,\frac{p^2}{2m} = \frac{2}{(2\pi\hbar)^3}\int d\underline{r}\int_{\text{disp. sphere}} d\underline{p}\,\frac{(\bar{p}+\bar{D})^2}{2m}$$

$$= \frac{2}{(2\pi\hbar)^3}\int d\underline{r}\int d\underline{p}\,\frac{(p^2+D^2+2\bar{p}\cdot\bar{D})}{2m} = \frac{1}{m\hbar^3}\int d\underline{r}\left(\frac{p_f^5}{10\pi^2}+\frac{p_f^3D^2}{6\pi^2}\right)$$

where the integral of $\bar{p}\cdot\bar{D}$ vanishes because of symmetry and the Fermi momentum P_f is related to the density $n(\underline{r})$ by

II. 5 $$n(\underline{r}) = \frac{p_f^3}{3\pi^2\hbar^3}$$

The potential energy is given by

II. 6 $$E_p = \frac{e^2}{2}\int d\underline{r}'\int d\underline{r}\,\frac{n(\bar{r})n(\bar{r}')}{|\underline{r}-\underline{r}'|} - e\int d\underline{r}\,V_N(\underline{r})$$

where $V_N(\underline{r})$ is the nuclear potential.

The first constraint on the system is

II. 7 $$N = \int n(\underline{r})d\underline{r} = \text{number of electrons}$$

and the second is

II. 8 $$Jh = \int (r\times D(\underline{r}))n(\underline{r})d\underline{r} = \int rD(\underline{r})\sin\theta\, n(\underline{r})d\underline{r}$$

where Jh is the angular momentum of the atom and $\bar{D}(\underline{r})$ has been chosen in the ϕ direction.

One now introduces the Lagrangian multipliers λ and μ on the conditions of angular momentum and particle number. Variation with respect to $\bar{D}(\underline{r})$ yields

II. 9 $$D(\underline{r}) = -\lambda m r \sin\theta$$

Variation with respect to $n(\underline{r})$ in conjunction with Poisson's equation yields the following equation for the potential in the atom;

II. 10 $$\nabla^2\Phi = \frac{4e^2}{3\pi\hbar^3}\left[2m(\Phi-\mu) + (\lambda m r \sin\theta)^2\right]^{3/2}$$

where

II. 10a $$\Phi(\underline{r}) = V_N(\underline{r}) - e\int\frac{n(\underline{r}')d\underline{r}'}{|\underline{r}-\underline{r}'|} = \text{potential at } \underline{r}$$

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. 10 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.

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, attempt to rederive the Sessler-Foley modification of 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 now given by

II. 11 $$E_K = \frac{2}{(2\pi\hbar)^3} \int d\underline{r} \int_{\text{Sphere}} d\underline{p}\, \frac{p^2}{2m} = \frac{1}{m\hbar^3} \int d\underline{r}\, \frac{P_f^5}{10\pi^2}$$

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

II. 12 $$E_p = \frac{e^2}{2} \int d\underline{r}' \int d\underline{r}\, \frac{n(\underline{r})n(\underline{r}')}{|\underline{r}'-\underline{r}|} - \int d\underline{r}\, n(\underline{r}) \left(eV_N(\underline{r}) - \frac{mr^2\omega^2}{2}\right)$$

The energy density E' is related to the energy density E of the non-rotating system by

II. 13 $$E' = E + n(\underline{r})\frac{mr^2\omega^2}{2}$$

We may therefore consider the quantity

II. 14 $$[mr^2\overline{\omega}]n(\underline{r})$$

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

II. 15
$$\int d\underline{r} \left(\frac{\hbar^2}{m} \frac{(3\pi^2)^{5/3}}{10\pi^2} [n(\underline{r})]^{5/3} + \frac{e^2}{2} \int d\underline{r}' \frac{n(\underline{r})n(\underline{r}')}{|r-r'|} - eV_N(\underline{r})n(\underline{r}) + \frac{mr^2\omega^2}{2} n(\underline{r}) \right.$$
$$+ \lambda \int d\underline{r}\, n(\underline{r}) mr^2 \bar{\omega} + \mu \int d\underline{r}\, n(\underline{r}) \, .$$

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

II. 16
$$\omega = -\lambda \mathrm{Sin}\ \theta$$

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

$$\nabla^2\phi = \frac{4e2}{3\pi\ \hbar^3} \left(2m(\phi-\mu) + [\lambda mr\mathrm{Sin}\ \theta]^2\right)^{3/2}$$

which is seen to be identical with II. 10.

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 in the following sections attempt to discover whether this is true in the case of the atom as well.

III - THE MIXED POSITION - ANGULAR MOMENTUM REPRESENTATION

We use the Green's function formalism introduced by Schwinger[9] 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,...N particle density matrices. In this formalism the N particle Green's function

$$G_N(r_1t_1 \ldots r_Nt_N : r_1't_1' \ldots r_N't_N')$$

is analogous to the N particle density matrix and contains the same information about the system.[10] 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

III. 1a $$H = \sum_i H_o(\underline{r}_i) + 1/2 \sum_{i \neq j} v(\underline{r}_i - \underline{r}_j)$$

III. 1b $$H_o(\underline{r}_i) = \frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{|\underline{r}_i|}$$

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

The first of the coupled hierarchy of integro-differential equations involving the one and two particle Green's functions is

III. 2 $$\left(i\hbar\frac{\partial}{\partial t_1} - H_o(\underline{r}_1)\right)G_1(\underline{r}_1 t_1 : \underline{r}_1' t_1') + i\int d\underline{r}_2\, v(\underline{r}_1-\underline{r}_2)G_2(\underline{r}_1 t_1 \underline{r}_2 t_1 : \underline{r}_1' t_1' \underline{r}_2 t_1^+)$$

$$= \hbar\delta(\underline{r}_1-\underline{r}_1')\delta(t_1-t_1')$$

where the coordinates in the arguments of the Green's functions are assumed to include spin direction as well as spatial position, and summation over the corresponding spin index is assumed to accompany integration over a coordinate.

We introduce the Hartree-Fock approximation by replacing the two particle Green's function by an antisymmetrized product of one particle Green's functions, i.e.

III. 3 $$G_2(\underline{r}_1 t_1 \underline{r}_2 t_2 : \underline{r}_1' t_1' \underline{r}_2' t_2') \simeq G_1(\underline{r}_1 t_1 : \underline{r}_1' t_1')G_1(\underline{r}_2 t_2 : \underline{r}_2' t_2') - G_1(\underline{r}_1 t_1 : \underline{r}_2' t_2')G_1(\underline{r}_2 t_2 : \underline{r}_1' t_1')$$

If we take note of the fact that in the absence of spin dependent forces a particle propagates without changing its spin we may insert III.3 in III.2 and perform the required summation over spin indices obtaining

III. 4 $$\left(i\hbar\frac{\partial}{\partial t_1} - H_o(\underline{r}_1)\right)G_1(\underline{r}_1 t_1 : \underline{r}_1' t_1')$$

$$+ i\int d\underline{r}_2\, v(\underline{r}_1-\underline{r}_2)\left(2G_1(\underline{r}_2 t_1 : \underline{r}_2 t_1^+)G_1(\underline{r}_1 t_1 : \underline{r}_1' t_1') - G_1(\underline{r}_1 t_1 : \underline{r}_2' t_1^+)G_1(\underline{r}_2 t_1 : \underline{r}_1' t_1')\right)$$

$$= \hbar\delta(\underline{r}_1-\underline{r}_1')\delta(t_1-t_1')$$

Following Baraff and Borowitz this may be written as a pair of integral equations:

III. 5a $$\int K(\underline{r}_1 t_1 : \underline{r}_2 t_2) d\underline{r}_2 dt_2 G_1(\underline{r}_2 t_2 \underline{r}_1' t_1') = \hbar\delta(\underline{r}-\underline{r}_1')\delta(t_1-t_1')$$

where the kernel $K(\underline{r}_1 t_1 : \underline{r}_2 t_2)$ is defined by

III. 5b $$K(\underline{r}_1 t_1 : \underline{r}_2 t_2) =$$

$$\left(i\hbar \frac{\partial}{\partial t_1} - H_o(\underline{r}_1) + 2i\int d\underline{r}' v(\underline{r}_1-\underline{r}') G_1(\underline{r}' t : \underline{r}' t^+)\right)\delta(\underline{r}_1-\underline{r}_2)\delta(t_1-t_2)$$

$$-iv(\underline{r}_1-\underline{r}_2) G_1(\underline{r}_1 t_1 : \underline{r}_2 t^+)\delta(t_1-t_1')$$

It is at this point that Baraff and Borowitz effect a transformation to a mixed position-momentum representation. For the description of an atom with non-vanishing 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 shall introduce a transform that makes use of the free particle solutions in spherical coordinates. The usefullness 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. Since the transform is somewhat unusual we shall describe it in detail.

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

III. 6 $$\hat{G}_{\ell m}(\underline{R}p\omega) = \int G_1(\underline{r}_1 t_1 \underline{r}_2 t_2)\Psi_{p\ell m}(\underline{r}_1) e^{\frac{i\omega}{\hbar}(t_1-t_2)} d\underline{r}_1 d(t_1-t_2)$$

where

III. 7 $$\Psi_{p\ell m}(\underline{r}) = (2\pi)^{3/2}\hbar/\sqrt{\hbar r}\; J_{\ell+1/2}\left(\frac{pr}{\hbar}\right) Y_{\ell m}(\theta,\phi)$$

where $J_{\ell+1/2}$ are cylindrical Bessel functions, the $Y_{\ell m}(\theta,\phi)$ are normalized spherical harmonics and

III. 8 $$\underline{R} = \frac{\underline{r}_1 + \underline{r}_2}{2}$$

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

Since the functions $\hat{G}_{\ell m}$ and G_1 have their time and energy dependence related through a Fourier transform, that part of the calculation of the inverse offers no difficulty. The inverse of the angular momentum dependence of $\hat{G}_{\ell m}$ is calculated by multiplying by the complex conjugate of $\Psi_{p\ell m}$ and integrating over the magnitude of the momentum and summing over all values of ℓ and m.

Thus we have from III. 6

III. 9 $$\sum_{\ell,m} \int \hat{G}_{\ell m}(\underline{R}p\omega)\, \Psi^*_{p\ell m}(\underline{r}_1{}')e^{\frac{-i\omega}{\hbar}(\tau_1'-t_2')}\, dp d\omega =$$

$$\sum_{\ell,m} G_1(\underline{r}_1 t_1 \underline{r}_2 t_2)\Psi_{p\ell m}(\underline{r}_1)\Psi^*_{p\ell m}(\underline{r}_1')e^{\frac{i\omega}{\hbar}(t_1-t_2)-(t_1'-t_2')}\, d\underline{r}_1' dp d\omega d(t_1-t_2)$$

The time and energy integrations may be done immediately yielding for the right hand side of III. 9

III. 10 $$2\pi\hbar\sum_{\ell m}\int G_1(\underline{r}_1 t_1' \underline{r}_2 t_2')\Psi_{p\ell m}(\underline{r}_1)\Psi^*_{p\ell m}(\underline{r}_1')d\underline{r}_1 dp$$

We may now perform the p integration by noting that[11]

$$\int J_m(kx)J_m(kx_o)kdk = \frac{\delta(x-x_o)}{\sqrt{xx_o}}$$

independent of the value of m.

The result of the p integration in III. 10 is

III. 11 $$(2\pi\hbar)^4 \sum_{\ell m} \int G_1(\underline{r}_1 t_1' \underline{r}_2 t_2') \frac{\delta(r_1-r_1')}{r_1 r_1'} r_1^2 dr_1 \; Y_{\ell m}(\theta_1\phi_1)Y^*_{\ell m}(\theta'_1\phi'_1)\sin\theta_1 d\theta_1 d\phi_1$$

Since the spatial integration is to be performed keeping $\underline{R}$ constant there is only one independent angle variable and we may expand the spatially dependent one particle Green's function as follows:

III. 12 $$G_1(\underline{r}_1 t_1' \underline{r}_2 t_2') = \sum_{uv} G_1^{uv}(r_1 t_1' r_2 t_2')Y^*_{uv}(\theta_1,\phi_1)$$

Expression III. 11 then becomes

III. 13 $$(2\pi\hbar)^4 \sum_{\substack{uv\\ \ell m}} \int G_1^{uv}(r_1 t_1' r_2 t_2') \frac{\delta(r_1-r_1')}{r_1 r_1'} r_1^2 dr_1 \; Y^*_{\ell m}(\theta_1'\phi_1')Y_{\ell m}(\theta_1\phi_1)Y^*_{uv}(\theta_1,\phi_1)\sin\theta_1 d\theta_1 d\phi$$

The spatial integrations may now be performed yielding

III. 14 $$(2\pi\hbar)^4 \sum_{\ell m} G_1^{\ell m}(r_1' t_1' r_2' t_2') \; Y^*_{\ell m}(\theta_1'\phi_1') = (2\pi\hbar)^4 G_1(r_1' t_1' r_2' t_2')$$

where use has been made of III. 12 in the last step.

The inverse transform is thus given by

$$\text{III. 15} \quad G_1(\underline{r}_1 t_1 \underline{r}_2 t_2) = \frac{1}{(2\pi\hbar)^4} \sum_{\ell m} \int \hat{G}_{\ell m}(\underline{R}p\omega)\, \Psi^*_{p\ell m}(\underline{r}_1) e^{\frac{-i\omega}{\hbar}(t_1-t_2)} dp d\omega$$

The spatial density of the electrons may now be expressed in a form that displays the usefulness of the mixed position-angular momentum representation. For the atom with non-zero angular momentum.

$$\text{III. 16a} \quad n(\underline{R}) = -iG_1(\underline{R}t\underline{R}t^+) = \sum_{\ell m} \int \frac{dp}{(2\pi\hbar)^3}\, n_{\ell m}(\underline{R}p)\, \Psi^*_{p\ell m}(\underline{R})$$

$$\text{III. 16b} \quad n_{\ell m}(\underline{R}p) = -i\int \hat{G}_{\ell m}(\underline{R}p\omega) \frac{d\omega}{2\pi\hbar}$$

Equations III. 16 suggest the following physical interpretation; the quantity $n_{\ell m}(\underline{R}, p)$ is a density in a phase space that is charac.. .ized by a momentum subspace with one continuous coordinate and two discrete indices indicating the symmetry properties of the angular momentum. Physically we shall interpret $n_{\ell m}(\underline{R},p)$ as giving both the spatial distribution as well as the angular momentum distribution of electrons in the atom.

The mixed Fourier-Hankel transform of equation III. 5a is taken with respect to $\underline{r}_1$ and $t_1-t'_1$ keeping $\underline{R} = \frac{\underline{r}_1+\underline{r}'_1}{2}$ constant. We obtain

$$\text{III. 17} \quad \int K(\underline{r}_1 t_1 \underline{r}_2 t_2) d\underline{r}_2 dt_2 G_1(\underline{r}_2 t_2 \underline{r}'_1 t'_1)\, \Psi_{p\ell m}(r_1) e^{\frac{i\omega}{\hbar}(t_1-t'_1)} d\underline{r}_1 d(t_1-t'_1) = \frac{\hbar}{8}\, \Psi_{p\ell m}(\underline{R})$$

The quantity $\Psi_{p\ell m}(\underline{r}_1)$ may be expanded in plane waves as follows[12]

III. 18 $$\Psi_{p\ell m}(\underline{r}) = \frac{|p|}{i^{\ell}} \int d\Omega_p e^{\frac{ip\cdot\underline{r}}{\hbar}} Y_{\ell m}(\Omega_p)$$

Inserting III. 17 in III. 18 and interchanging the order of integration we obtain

III. 19 $$\frac{\hbar}{8}\Psi_{p\ell m}(\underline{R}) = \int K(\underline{r}_1 t_1 \underline{r}_2 t_2) d\underline{r}_2 dt_2 G_1(\underline{r}_2 t_2 \underline{r}_1' t_1') \Psi_{p\ell m}(\underline{r}_1) e^{\frac{i\omega}{\hbar}(t_1-t_1')} d\underline{r}_1 d(t_1-t_1')$$

$$= \frac{p}{i^{\ell}} \int d\Omega_p Y_{\ell m}(\Omega_p) \int K(\underline{r}_1 t_2 \underline{r}_2 t_2) d\underline{r}_2 dt_2 G_1(\underline{r}_2 t_2 \underline{r}_1' t_1') e^{\frac{ipr}{\hbar}+\frac{i\omega}{\hbar}(t_1-t_1')} d\underline{r}_1 d(t_1-t_1') \equiv \frac{p}{i^{\ell}} \int d\Omega_p Y_{\ell m}(\Omega_p) \tilde{KG}$$

where $\tilde{KG}$ is a Fourier transform defined by the above integral. This relationship between the Fourier transform $\tilde{KG}_p$ and the Hankel transform $\hat{KG}_{p\ell m}$ is quite general, i.e.

III. 20a $$\hat{KG}_{p\ell m} = \frac{p}{i^{\ell}} \int d\Omega_p \, Y_{\ell m}(\Omega_p) \, \tilde{KG}_p$$

III. 20b $$\tilde{KG}_p = \sum_{\ell m} \frac{i^{\ell}}{p} Y^*_{\ell m}(\Omega_p) \, \hat{KG}_{p\ell m}$$

Baraff and Borowitz have shown that the Fourier transform $\tilde{KG}$ 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. 19 becomes

III. 21 $$\frac{\hbar^{-3}}{8}\Psi_{p\ell m}(\underline{R}) = \frac{p}{i^{\ell}} \int d\Omega_p Y_{\ell m}(\Omega_p) \tilde{K}_o \tilde{G}_o = \frac{p}{i^{\ell}} \int d\Omega_p Y_{\ell m}(\Omega_p) \tilde{K}_o \left(\sum_{\lambda\mu} \frac{i^{\lambda}}{p} Y_{\lambda\mu}(\Omega_p) \hat{G}_{o\lambda\mu} \right)$$

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.

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 shall 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.

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 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 and since the distribution of a finite number of random variables each of which is Gaussian distributed 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. Chandrasekhar[14] gives as the probability distribution of the sum of a large number N individual random steps of mean square size $\overline{\ell^2}$

III. 22 $$W(L) = \frac{\exp\left(\frac{-L^2}{2N\ell^2}\right)}{\left(2N\ell^2\right)^{3/2}}$$

The variance of the distribution is .

III. 23 $$\sigma = \sqrt{N \cdot \overline{\ell^2}}$$

while the maximum possible angular momentum is

III. 24 $$L_{max} = N \sqrt{\overline{\ell^2}}$$

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

III. 25 $$\frac{\sigma}{L_{max}} = N^{-1/2}$$

We shall therefore, in attempting to describe the situation in which many electrons contribute to the angular momentum consider only the spherically symmetric term in III. 15 and in the sum on the right hand side of III. 21.

In that case III. 21 becomes

III. 26 $$\frac{\hbar^{-3}}{8} \Psi_{p\ell m}(\underline{R}) = \frac{G_{000}}{4\pi p} \frac{p}{i^{\ell}} \int d\Omega_p Y_{\ell m}(\Omega_p) \tilde{K}_o = \frac{\hat{G}_{000}\hat{K}_{o\ell m}}{4\pi p}$$

where

III. 27 $$\hat{K}_{o\ell m}(\underline{R}p\omega) = \left(\omega - \frac{p_R^2}{2m} - \frac{\ell(\ell+1)t^2}{2mR^2} + \frac{Ze^2}{|R|} - 2\int v(\underline{R}-\underline{r}) n_{000}(\underline{r}) d\underline{r}\right) \frac{\Psi_{p\ell m}(\underline{R})}{8}$$

$$\equiv \left(\omega - E(\underline{R}p\ell)\right) \frac{\Psi_{p\ell m}(\underline{R})}{8}$$

The zeroth order density $n_{ooo}(\underline{R},p)$ is related to $G_{ooo}(\underline{R},p)$ by

III. 28a $$n_{ooo}(\underline{R}p) = -i\int \frac{d\omega}{2\pi} e^{i\omega o^+} \hat{G}_{ooo}(\underline{R}p\omega)$$

and

III. 28b $$n_{ooo}(\underline{R}) = \int \frac{dp}{(2\pi)^3} \; n_{ooo}(\underline{R},p) \; \psi^*_{poo} \; (\underline{R})$$

We have therefore,

III. 29 $$\hat{G}_{ooo}(\underline{R},p\omega) = \frac{\hbar^{-3} 4\pi |p|}{\omega - E(\underline{R}p\ell)}$$

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 $\omega=\mu$ 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

III. 30a $$n_{ooo}(\underline{R},p) = 4\pi p\hbar^{-3} \qquad E(\underline{R}p\ell)<\mu$$

III. 30b $$= 0 \qquad E(\underline{R}p\ell)<\mu$$

The spatial density may be obtained from $n_{ooo}(\underline{R},p)$ by means of

equation III. 28b which yields

$$\text{III. 31} \qquad n_{ooo}(\underline{R}) = \frac{1}{6\pi^2\hbar^3}\left(2m(\mu-\phi) - \frac{\ell(\ell+1)\hbar^2}{R^2}\right)^{3/2}$$

where

$$\text{III. 32} \qquad \phi(\underline{R}) = \frac{-Ze^2}{R} + 2\int v(\underline{R}-\underline{r})n_{ooo}(\underline{r})d\underline{r}$$

Equation III. 31 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 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. 31. To bring the model into coincidence with the Sessler-Foley model we shall choose ℓ such that

$$J(J+1)\hbar^2 = \int \ell(\ell+1)\hbar^2 n_{ooo}(\underline{R})d\underline{R}$$

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

As pointed out by Sessler and Foley, this model corresponds to 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 angular momentum is given by

$$\text{III. 33} \quad -i\int \lim_{1'\to 1} L^2(1)G_1(11')d(1)+\frac{(-i)^2}{2}\int \lim_{\substack{1'\to 1\\ 2'\to 2}} 2L(1)-L(2)\big(G_1(11')G_1(22')-G_1(21')G_1(12')\big)d(1)d(2)$$

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.,

$$\text{III. 34} \quad G_1(\underline{r}_1 t_1 \underline{r}_2 t_2)=\frac{1}{(2\pi\hbar)^4}\int \hat{G}_{oo}(\underline{R}p\omega)\Psi^*_{poo}(\underline{R})e^{\frac{-i\omega}{\hbar}(t_1-t_2)}dpd\omega$$

If III. 34 is inserted in III. 33 the expectation value of the angular momentum is found to vanish because of the zero eigenvalue of the angular part of $\Psi^*_{poo}(\underline{R})$.

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 theoram derived 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 fornalism this amounts to choosing a more appropriate approximation than $\hat{G}_{oo}(\underline{R}p\omega)$ 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

III. 35a $$G_1(\underline{r}_1 t_1 \underline{r}_2 t_2) = G_1^{o}(\underline{r}_1 t_1 \underline{r}_2 t_2) + G_1^{L}(\underline{r}_1 t_1 \underline{r}_2 t_2)$$

where

III. 35b $$G_1^{o}(\underline{r}_1 t_1 \underline{r}_2 t_2) = \frac{1}{(2\pi\hbar)^4}\int \hat{G}_{oo}(\underline{R}p\omega)\Psi^{*}_{poo}(\underline{r}_1)e^{\frac{-i\omega}{\hbar}(t_1-t_2)}dpd\omega$$

and

III. 35c $$G_1^{L}(\underline{r}_1 t_1 \underline{r}_2 t_2) = \frac{1}{(2\pi\hbar)^4}\int \hat{G}_{Lm}(\underline{R}p\omega)\Psi^{*}_{pLm}(\underline{r}_1)e^{\frac{-i\omega}{\hbar}(t_1-t_2)}dpd\omega$$

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

III. 36a $$-i\int G_1(\underline{r}_1 t_1 : \underline{r}_1 t_1^{+})d\underline{r}_1 = N$$

a suitable normalization on the quantities just introduced is given by

III. 36b $$-i\int G_1^{o}(\underline{r}_1 t_1 ; \underline{r}_1 t_1^{+})d\underline{r} = N-n \qquad n=0,1,2,3$$

III. 36c $$-i\int G_1^{L}(\underline{r}_1 t_1 : \underline{r}_1 t_1^{+})d\underline{r} = n$$

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

III. 37a $$G_2(11':22') = G_2^{o}(11':22') + G_2^{L}(11':22')$$

where

III. 37b $$G_2^{o}(11':22') = \frac{1}{(2\pi\hbar)^8}\int G_2(\underline{R}poo : \underline{R}'p'oo\omega')\psi^{*}_{poo}(\underline{r}_1)\psi^{*}_{p'oo}(\underline{r}_2)e^{\frac{-i\omega}{\hbar}(t_1-t_1')-\frac{i\omega'}{\hbar}(t_2-t_2')}dpdp'd\omega d\omega'$$

and

III. 37c $$G_2^{L}(11':22') = \frac{1}{(2\pi\hbar)^8}\sum_{mm'LL} C(L,M,mm')\int G_2(\underline{R}pLm\omega : \underline{R}'p'Lm'\omega')\psi^{*}_{pLm}(\underline{r}_1)\psi^{*}_{p'Lm'}(\underline{r}_2)e^{\frac{-i\omega}{\hbar}(t_1-t_1')-\frac{i\omega'}{\hbar}(t_2-t_2')}dpdp'd\omega d\omega'$$

The C_{LL} appearing in III. 37 are Clebsch-Gordon coefficients.

In choosing appropriate normalizations for the two terms in III. 37a, we observe that the normalization of the two particle Green's function should be

III. 38 $$\frac{(-i)^2}{2}\int G_2(11:22)d(1)d(2) = \frac{N(N-1)}{2}$$

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:

III. 39a $$\frac{(-i)^2}{2}\int G_2^{o}(11:22)d(1)d(2) = \frac{(N-n)(N-n-1)}{2}$$

and

III. 39b $$\frac{(-i)^2}{2}\int G_2^{L}(11:22)d(1)d(2) = \frac{n(n-1)}{2}$$

This normalization corresponds to the separate anti-symmetrization of the core and the contents of the outer shell.

If we apply III. 33 to the forms of the one and two particle Green's functions chosen here we obtain

$$\text{III. 40} \quad -i\int \lim_{1'\to 1} L^2(1)\left(G_1^{o}(11')+G_1^{L}(11')\right)d(1)+\frac{(-i)^2}{2}\int \lim_{\substack{1'\to 1\\ 2'\to 2}} 2L(1)\cdot L(2)\left(G_2^{o}(11'22')+G_2^{L}(11'22')\right)d(1)d(2)$$

Substituting III. 35 and III. 37 in III. 40 and remembering that

$$L^2-L_1{}^2-L_2{}^2 = 2L_1\cdot L_2$$

we obtain

$$\text{III. 41} \quad \hbar^2 L(L+1)\left(-i\int G_1^{L}(11)d(1)\right)-\hbar^2 L(L+1)\frac{(-i)^2}{2}\int G_2(1122)d(1)d(2)$$

$$= L(L+1)\hbar^2\left(n-\frac{n(n-1)}{2}\right)$$

We thus obtain a zero angular momentum for the case of no electrons outside a spherical core and an angular momentum of $L(L+1)\hbar^2$ for 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 electrons outside a spherical core which combine to give an S state for the ground state.

Having found a form for the one particle Green's function 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. 31 becomes

$$\text{III. 42} \quad \frac{p}{iL}\int d\Omega_p Y_{Lm}(\Omega_p)\hat{K}_o(\hat{G}_o^o+\hat{G}_o^L) = \frac{\hbar^{-3}}{8}\Psi_{pLm}(\underline{R})$$

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

$$\text{III. 43} \quad \frac{p}{iL}\int d\Omega_p Y_{Lm}(\Omega_p)\tilde{K}_o\tilde{G}_o = \frac{\hat{K}_{oLm}\hat{G}_{ooo}}{4\pi p} = \frac{(\omega-E(\underline{R}pL))\,\Psi_{pLm}(\underline{R})\hat{G}_{ooo}(\underline{R},p\omega)}{4\pi p\quad 8}$$

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

$$\text{III. 20b} \quad \tilde{G}_o^L(\underline{R}p\omega) = \sum_{\lambda\mu}\frac{i^\lambda}{p}Y^*_{\lambda\mu}(\Omega_p)\hat{G}^L_{o\lambda\mu}(\underline{R}p\omega) = \frac{i^L}{p}Y^*_{Lm}(\Omega_p)\hat{G}^L_{oLm}(\underline{R}p\omega)$$

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

$$\text{III. 44} \quad Y_{\ell m}(\Omega_p)Y^*_{\ell m}(\Omega_p)=\sum_{\lambda\mu}\frac{(-)^m(2\ell+1)}{\sqrt{4\pi}\,\sqrt{2\ell+1}}C_{\ell\ell}(\lambda ooo)C_{\ell\ell}(\lambda\mu,m,-m)Y_{\lambda\mu}(\Omega_p)\equiv\sum_{\lambda\mu}B^{\lambda\mu}_{Lm}Y_{\lambda\mu}(\Omega_p)$$

where the $C_{\ell\ell}$ are the usual Clebsch-Gordon coefficients. Inserting III. 20b, III. 44 in III. 42 yields for the second integral in the latter equation

$$\text{III. 45} \quad \frac{p}{iL}\int d\Omega_p Y_{Lm}(\Omega_p)\tilde{K}_o\tilde{G}_o^L = \hat{G}_{oLm}\frac{i^L}{p}\sum_{\lambda\mu}B^{\lambda\mu}_{Lm}\hat{K}_{o\lambda\mu}(\underline{R}p\omega)$$

$$= \hat{G}_{oLm}\frac{i^L}{8p}\sum_{\lambda\mu}B^{\lambda\mu}_{Lm}\Psi_{p\lambda\mu}(\underline{R})(\omega-\overline{E})$$

where

III. 45a $$\bar{E} = \frac{\sum_{\lambda\mu} E(\underline{R},p,\lambda) B^{\lambda\mu}_{Lm} \psi_{p\lambda\mu}(\underline{R})}{\sum_{\lambda\mu} B^{\mu}_{Lm} \psi_{p\lambda\mu}(\underline{R})}$$

Thus eq. III. 42 becomes

III. 46 $$\frac{\hat{G}_{ooo}(\underline{R}p\omega)}{4\pi p} + \frac{\hat{G}_{oLm}(\underline{R}p\omega) i^{L}}{p} \cdot \frac{\sum_{\mu} B^{\lambda\mu}_{Lm} \psi_{p\lambda\mu}(\underline{R})}{\psi_{pLm}(\underline{R})} \left(\frac{\omega-\bar{E}}{\omega-\bar{E}}\right) = \frac{\hbar^{-3}}{\omega-E(\underline{R}pL)}$$

Since $\hat{G}_{ooo}$ is of the order of N times larger than $\hat{G}_{oLm}$ we may solve first for the core density in the absence of the outer electrons obtaining as in III. 29 (the Sessler-Foley model)

III. 47 $$\hat{G}_{ooo}(\underline{R}p\omega) = \frac{\hbar^{-3} 4\pi p}{\omega-E(\underline{R},pL)}$$

Since the functional variation of $\hat{G}_{ooo}(\underline{R}p\omega)$ for N-n particles is the same as for the N in the Sessler-Foley model we may write III. 46 as

III. 48a $$\hat{G}_{oLm}(\underline{R}p\omega) \frac{i^{L} \sum_{\lambda\mu} B^{\lambda\mu}_{Lm} \psi_{p\lambda\mu}(\underline{R})}{\psi_{pLm}(\underline{R})} = \frac{n}{N} \cdot \frac{\hbar^{-3}}{\omega-\bar{E}}$$

and

III. 48b $$\hat{G}_{ooo}(\underline{R}p\omega) = \frac{N-n}{N} \cdot \frac{\hbar^{-3} 4\pi p}{\omega-E}$$

Integrating as before over the complex energy plane we obtain

III. 49a $$n_{oLm}(\underline{R},p) = \frac{4\pi p \hbar^{-3} n}{N} \cdot \frac{\psi_{pLm}(\underline{R})}{4\pi i^{L} \sum_{\lambda\mu} B^{\lambda\mu}_{Lm} \psi_{p\lambda\mu}(\underline{R})} \quad ; \bar{E} < \mu$$

III. 49b $$n_{ooo}(\underline{R},p) = \frac{N-n}{N} \cdot 4\pi p\hbar^{-3} \quad ; \quad E < \mu$$

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

III. 50 $$n_{ooo}(\underline{R}) = \int_{o}^{P_{max}} \frac{dp}{(2\pi)^3} \frac{N-n}{N} \cdot 4\pi p\hbar^{-3} \psi^*_{poo}(\underline{R}) = \frac{N-n}{N} \frac{1}{6\pi^2\hbar^3}\left(2m(\mu-\phi) - \frac{L(L+1)\hbar^2}{R^2}\right)^{3/2}$$

to lowest order in $\hbar$.

We may obtain a spatial density from III. 49a that corresponds to what one might expect on physical grounds by approximating the denominator by $\psi_{poo}(\underline{R})$. In that case

III. 51 $$n_{oLm}(\underline{R}) = \int_{o}^{P_{max}} \frac{4\pi\hbar^{-3}np}{N} \frac{\psi_{pLm}\psi^*_{pLm}}{\psi_{poo}} dp = \frac{R^{2L}Y^2_{Lm}\left(2m(\mu-\phi) - \frac{L(L+1)\hbar^2}{R^2}\right)^{\frac{2L+3}{2}}}{2\pi^2(2L+3)\hbar^{2L+3}} \frac{n}{N}$$

to lowest order in $\hbar$. 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 $n \to -n$ in III. 36 and III. 39 thereby obtaining for the expectation value of the angular momentum in III. 41

III. 52 $$L(L+1)\hbar^2 \left(-n - \frac{n(n+1)}{2}\right)$$

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 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

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

The importance of this quantity lies in the fact that the quadrupole moment of the nucleus is not measured directly but rather through a quadrupole splitting in atomic spectra. The relationship between the quadrupole coupling constant and the measured quadrupole splitting is

IV. 2 $$hb = e^2qQ$$

where Q is the nuclear quadrupole moment and b is the measured frequency of the splitting.

For the case of the quadrupole coupling constant 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. 35a 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. 51 we obtain for the case of the halogens

$$\text{IV. 3} \qquad q = \frac{\langle 3\cos^2\theta - 1\rangle_{P_{3/2}}}{2\pi^2\hbar^{2L+3}(2L+3)Z} \int_{R_{min}}^{\infty} R^{2L-1}\, {}_{2m\phi}^{\frac{2L+3}{2}}\, dR$$

The expectation value of $3\cos^2\theta-1$ in the ground $P_{3/2}$ state of the halogens is -2/5. Noting that for the present case L=1 and transforming to universal Thomas-Fermi coordinates we obtain

$$\text{IV. 4} \qquad q = \frac{-4\sqrt{2}}{25\pi^2} \cdot \frac{Z^{5/3}}{a_o^3} \int_{x_{min}}^{\infty} X^{5/2}(x)x^{3/2}dx$$

In order to arrive at a reasonable lower limit for the integration we note that the lowest limit of the validity of the Thomas-Fermi model is $a_o/Z^{1.6}$, which is the radius of the first Bohr orbit in the field of a nucleus of charge Ze. That very little is 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_o. The charge inside a sphere of radius a_o in this case is approximately .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_o/Z as a lower limit we obtain for the quadrupole coupling constants of the halogens

$$q_{Cl}a_o^3 = -2.4$$

$$q_{Br}a_o^3 = -21.$$

$$q_I a_o^3 = -51.$$

These figures are within an order of magnitude of the accepted values, the value for chlorine being in good agreement with the accepted value and that for iodine six times too large. The value of $|q|$ however is seen to increase with Z in contrast to the Sessler-Foley model where it varies as $Z^{-2/3}$.

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. SUMMARY AND CONCLUSION

We have shown how the inclusion of additional information in a statistical model can lead to more desirable results. In particular in the case of the atom with angular momentum the specification of the internal structure leads to a model that differs from the Sessler-Foley result.

We believe that the present model offers a better starting form for the density in detailed self-consistent machine calculations of atomic structure. In addition, the model should prove useful in investigating at least the qualitative properties of the atom that vary in the characteristic way of the periodic table.

It is also anticipated that the approach used in the present paper may be utilized fruitfully in any self-consistent statistical model of the nucleus.

More generally, however, we feel that any statistical treatment of a physical system may be improved if a suitable formalism is found in which empirical information about the system may be inserted.

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 $2\ell+1$ integral values between ℓ and $-\ell$. 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

$$\omega_n = \frac{\sum_{i=1}^{n} \mu_{2+\delta}^{(i)}}{B_n^{1+\delta/2}} \xrightarrow[n\to\infty]{} 0$$

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

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

The third absolute moment exists since

$$\mu_3 = \sum_k |k^3| f(k) = \sum_{k,m} \frac{1}{2\ell+1} |k^3| \delta_{mk}$$

$$= \frac{1}{2\ell+1} \sum_{m=-\ell}^{\ell} |m^3| = \frac{2}{2\ell+1} \sum_{m=0}^{\ell} m^3 = \frac{2}{2\ell+1} \left(\frac{\ell(\ell+1)}{2}\right)^2$$

The mean square fluctuation of k_i is

$$\overline{\Delta k_i^2} = \overline{k_i^2} - \overline{k_i}^2$$

$$\overline{k_i} = \sum_k k_i f(k_i) = \sum_{k,m} k_i \frac{\delta mki}{2\ell+1} = \sum_{m=-\ell}^{\ell} \frac{m}{2\ell+1} = 0$$

$$\overline{k_i^2} = \sum_k k_i^2 f(k_i) = \sum_{k,m} k_i^2 \frac{\delta mki}{2\ell+1} = \sum_{m=-\ell}^{\ell} \frac{m^2}{2\ell+1} =$$

$$= \frac{2}{2\ell+1} \sum_{m=0}^{\ell} m^2 = \frac{\ell(\ell+1)}{3}$$

Thus $\overline{\Delta k_i^2} = \frac{\ell(\ell+1)}{3}$ and

$$B_n = n\overline{\Delta k_i^2} = \frac{n\ell(\ell+1)}{3}$$

The quotient ω_n therefore becomes

$$\omega_n = \frac{2}{2\ell+1} \frac{\left(\frac{\ell(\ell+1)}{2}\right)^2}{\left(\frac{\ell(\ell+1)}{3}\right)^{3/2}} \cdot \frac{n}{n^{3/2}}$$

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.

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