VIBRATIONAL-ROTATIONAL EFFECTS

ON THE

NUCLEAR MAGNETIC SHIELDING CONSTANT

IN THE

H_2, HD, AND D_2 MOLECULES

by

Robert R. Gilman

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ABSTRACT

Nuclear shielding theory is reviewed. General expressions are developed for the shielding using an extension of the Chan-Das formalism, including vibration and rotation. The James-Coolidge wave functions by Kolos and Roothaan for H_2 are employed. The electronic integrals for the diamagnetic part of the shielding are reduced to well-known functions. Flowcharts are presented to outline machine computation.

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I cannot adequately express my indebtedness and my sincere thanks to Dr. Sunney I. Chan for his informative discussions, especially of the physics of the problem, his patience, and the opportunities to learn which he has made available. I am especially grateful for the interest and desire he has stimulated. Two of his special comments:

"You'd better think about it."

"Are you sure you want to be a theoretician?"

Credit for the reduction of the electronic integrals is due to Klaus Rudenberg. Reductions are much easier the second time.

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I - Introduction

The techniques of Nuclear Magnetic Resonance Spectroscopy have been developed to the stage where vibrational effects on proton chemical shifts have been detected experimentally in many molecules. These experimental results are of fundamental importance in that they allow one to monitor the variations of the electronic charge distribution with vibrational motion. In view of the fact that accurate electronic wave functions are now available for several diatomic molecules at various internuclear distances, _ab-initio_ calculations of these effects are quite feasible. The precision with which one can predict the observed vibrational effects not only serves to check the accuracy of the electronic wave functions at these internuclear distances, but also provides a test of the validity of several approximate methods presently used to calculate magnetic properties.

This thesis is concerned with the evaluation of the proton magnetic shielding constant in H_2, HD, and D_2. Several sets of accurate electronic wave functions are available for H_2. These are Kolos and Roothaan's 28-, 40-, and 50-term variational functions[1] and Fraga and Ransil's LCAO-MO functions with configuration interaction.[2] Recently Chan and co-workers[3] have employed the functions of Kolos and Roothaan in a calculation of the rotational magnetic moments. The computed variation of the rotational moments with isotopic mass and vibrational state was in excellent agreement with experiment. In addition, these investigators presented accurate vibrational-rotational wave functions suitable for application to the present problem. The necessary vibration-rotation integrals have been evaluated.

In the present work the wave functions of Kolos and Roothaan will be employed in the evaluation of the diamagnetic shielding. The so-called ground-state contribution to the paramagnetic term of the shielding will be obtained by the use of a modification of the method of Chan and Das[(4)] to include the effects of zero-point motion. A one-parameter variational calculation will be undertaken to estimate the excited-state contribution to the paramagnetic shielding. This separation of the shielding may appear somewhat arbitrary; however, it allows one to investigate the effects of vibrational motion on each of these terms in a convenient way. The paramagnetic contribution is expected to be particularly sensitive to vibrational-rotational effects since this part of the nuclear shielding is extremely sensitive to changes in the shape of the charge distribution. It is hoped that the present calculations will illustrate this in a quantitative way.

This thesis summarizes that part of the work completed at the time of writing. The theory of diamagnetic and paramagnetic shielding will be reviewed. The electronic integrals for the diamagnetic term will be reduced to well-known functions in considerable detail. Flowcharts will then be presented to outline the evaluation of the integrals by high-speed computer. At present no numerical calculations have been done.

II - Review of magnetic shielding theory

For a molecule in the absence of magnetic fields we may write the approximate Hamiltonian

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{electronic} + \hat{\mathcal{H}}_{nuclear} \tag{1.1}$$

where

$$\hat{\mathcal{H}}_{electronic} = \sum_{\substack{k \\ electrons}} \frac{p_k^2}{2m_e} + \sum_{\substack{n\ nuclei \\ k\ electrons}} \frac{Z_n e}{r_{kn}} + \sum_{\substack{i<k \\ electrons}} \frac{e^2}{r_{ik}}$$

$$\hat{\mathcal{H}}_{nuclear} = \sum_{n\ nuclei} \frac{p_n^2}{2M_n} + \sum_{\substack{j<n \\ nuclei}} \frac{Z_j Z_n}{r_{jn}}$$

Here $\underline{r}_{ab}$ is the vector from particle 'b' to particle 'a' ('i' and 'k' refer to electrons, 'n' and 'j' to nuclei) and Z_n is the charge on nucleus 'n' of mass M_n.

In the presence of magnetic fields the Hamiltonian is modified by the addition of

$$\hat{\mathcal{H}}_{field} = \sum_{k\ electrons} \left(\frac{e^2}{2mc^2} \underline{A}_k^2 - \frac{e}{mc} \underline{A}_k \cdot \underline{p}_k - \underline{\mu}_k \cdot \underline{H}_0 \right)$$

$$+ \sum_{\substack{n \\ nuclei}} \left(\frac{Z_n^2}{2M_n c^2} \underline{A}_n^2 - \frac{Z_n}{M_n c} \underline{A}_n \cdot \underline{p}_n - \underline{\mu}_n \cdot \underline{H}_0 \right) \tag{1.2}$$

where $\underline{A}_p$ is the magnetic vector potential at particle 'p'. We may write

$$\underline{A}_n = \frac{1}{2} \underline{H}_0 \times \underline{r}_{no} + \sum_{k\ electrons} \frac{\underline{\mu}_k \times \underline{r}_{nk}}{r_{nk}^3} + \sum_{j \neq n\ nuclei} \frac{\underline{\mu}_j \times \underline{r}_{nj}}{r_{nj}^3}$$

$$\underline{A}_k = \frac{1}{2} \underline{H}_0 \times \underline{r}_{ko} + \sum_{\substack{i \neq k \\ electrons}} \frac{\underline{\mu}_i \times \underline{r}_{ki}}{r_{ki}^3} + \sum_{\substack{n \\ nuclei}} \frac{\underline{\mu}_n \times \underline{r}_{kn}}{r_{kn}^3} \tag{1.3}$$

where $\underline{\mu}_p$ is the magnetic dipole moment of particle 'p' and $\underline{H}_o$ is an external magnetic field. In the following calculations we will treat $\hat{\mathcal{H}}_{field}$ as a perturbation to $\hat{\mathcal{H}}_o$.[5] Since, for any nucleus of interest the spin-interaction energy in the external field may be written[6]

$$E_{int} = -\underline{\mu}_N \cdot (\underset{\sim}{I} - \underset{\sim}{\sigma}_N) \cdot \underline{H}_o \tag{1.4}$$

where $\underset{\sim}{\sigma}_N$ is the shielding tensor (assumed independent of $\underline{\mu}_N$ and $\underline{H}_o$), we will be interested only in terms in the energy proportional to $\underline{\mu}_N$ and $\underline{H}_o$. Neglecting electron spin, substituting eq. 1.3 into eq. 1.2 yields

$$\begin{aligned}\hat{\mathcal{H}}_{field} = &\sum_{k\ \text{electrons}} \frac{e^2}{2mc^2}\left[\frac{1}{2}\underline{H}_o \times \underline{r}_{ko} + \sum_{\substack{n\\ \text{nuclei}}} \frac{\underline{\mu}_n \times \underline{r}_{kn}}{r_{kn}^3}\right]^2 \\ &- \sum_{k\ \text{electrons}} \frac{e}{mc}\left[\frac{1}{2}\underline{H}_o \times \underline{r}_{ko} \cdot \underline{p}_k + \sum_{\substack{n\\ \text{nuclei}}} \frac{\underline{\mu}_n \times \underline{r}_{kn}}{r_{kn}^3} \cdot \underline{p}_k\right] \\ &+ \sum_{\substack{n\\ \text{nuclei}}} \frac{Z_n^2}{2M_nc^2}\left[\frac{1}{2}\underline{H}_o \times \underline{r}_{no} + \sum_{\substack{j\neq n\\ \text{nuclei}}} \frac{\underline{\mu}_j \times \underline{r}_{nj}}{r_{nj}^3}\right]^2 \\ &- \sum_{n\ \text{nuclei}} \left\{\frac{Z_n}{M_nc}\left[\frac{1}{2}\underline{H}_o \times \underline{r}_{no} \cdot \underline{p}_n + \sum_{\substack{j\neq n\\ \text{nuclei}}} \frac{\underline{\mu}_j \times \underline{r}_{nj}}{r_{nj}^3} \cdot \underline{p}_n\right] + \underline{\mu}_n \cdot \underline{H}_o\right\}\end{aligned} \tag{1.5}$$

We now note that $\hat{\mathcal{H}}_{field}$ can be expressed as a sum of terms in H_o, $\mu_N H_o$, H_o^2, etc., where 'N' refers to the nucleus of interest:

$$\hat{\mathcal{H}}_{field} = \hat{\mathcal{H}}_f(H_o) + \hat{\mathcal{H}}_f(\mu_N H_o) + \hat{\mathcal{H}}_f(\mu_N) + \hat{\mathcal{H}}_f(H_o^2) + \cdots\cdots \tag{1.6}$$

If we express the first-order perturbation to the zero-order wave function Ψ_0 as $\underline{H}_0 \cdot \underline{\Psi}_1$, we have for the total wave function

$$\Psi = \frac{1}{\sqrt{N}}\left(\Psi_0 + \underline{H}_0 \cdot \underline{\Psi}_1 + \text{ higher orders in } \underline{H}_0\right) \tag{1.7}$$

$$N = 1 + \langle \underline{H}_0 \cdot \underline{\Psi}_1^* | \Psi_0 \rangle + \langle \Psi_0^* | \underline{H}_0 \cdot \underline{\Psi}_1 \rangle + \langle \underline{H}_0 \cdot \underline{\Psi}_1^* | \underline{H}_0 \cdot \underline{\Psi}_1 \rangle + \cdots$$

Hence terms in the energy proportional to $\mu_N H_0$ are given by

$$E(\mu_N H_0) = \langle \Psi_0 | \hat{\mathcal{H}}_f(\mu_N H_0) | \Psi_0 \rangle \frac{1}{N} + \frac{2}{N} \langle \Psi_0 | \hat{\mathcal{H}}_f(\mu_N) | \underline{H}_0 \cdot \underline{\Psi}_1 \rangle \tag{1.8}$$

Collecting terms from eq. 1.5 yields

$$\hat{\mathcal{H}}_f(\mu_N) = -\sum_{k \text{ electrons}} \frac{e}{mc} \frac{\underline{\mu}_N \times \underline{r}_{kN}}{r_{kN}^3} \cdot \underline{p}_k - \sum_{\substack{n \neq N \\ \text{nuclei}}} \frac{Z_n}{M_n c} \frac{\underline{\mu}_N \times \underline{r}_{nN}}{r_{nN}^3} \cdot \underline{p}_n$$

$$\hat{\mathcal{H}}_f(\mu_N H_0) = \sum_{k \text{ electrons}} \frac{e^2}{2mc^2} \underline{H}_0 \times \underline{r}_{k0} \cdot \frac{\underline{\mu}_N \times \underline{r}_{kN}}{r_{kN}^3} - \underline{\mu}_N \cdot \underline{H}_0$$

$$+ \sum_{\substack{n \neq N \\ \text{nuclei}}} \frac{Z_n^2}{2M_n c^2} \underline{H}_0 \times \underline{r}_{k0} \cdot \frac{\underline{\mu}_N \times \underline{r}_{nN}}{r_{nN}^3} \tag{1.9}$$

where the electron coupled spin-spin interaction has been dropped.

We now note that

$$\underline{\mu}_N \times \underline{r}_{kN} \cdot \underline{p}_k = \underline{\mu}_N \cdot \underline{r}_{kN} \times \underline{p}_k = \underline{\mu}_N \cdot \hat{\underline{\ell}}_{kN}$$

where $\hat{\underline{\ell}}_{kN}$ is the angular momentum operator for particle 'k' about 'N'. We then have, from eqs. 1.4 and 1.8,

$$E_{int} = -\underline{\mu}_N \cdot (\underset{\sim}{I} - \underset{\sim}{\sigma}_N) \cdot \underline{H}_0 = -\underline{\mu}_N \cdot \underline{H}_0 + \underline{\mu}_N \cdot \underset{\sim}{\sigma}_N \cdot H_0$$

$$= \frac{1}{N} \langle \Psi_0 | \sum_k \frac{e^2}{2mc^2} \underline{H}_0 \times \underline{r}_{k0} \cdot \frac{(\underline{\mu}_N \times \underline{r}_{kN})}{r_{kN}^3} | \Psi_0 \rangle - \underline{\mu}_N \cdot \underline{H}_0$$

$$+ \frac{1}{N} \langle \Psi_0 | \sum_{n \neq N} \frac{Z_n^2}{2M_n c^2} \underline{H}_0 \times \underline{r}_{n0} \cdot \frac{(\underline{\mu}_N \times \underline{r}_{nN})}{r_{nN}^3} | \Psi_0 \rangle$$

$$-\frac{1}{N}\sum_{k}\frac{2e}{mc}\left\langle\psi_0\left|\underline{\mu}_N\cdot\frac{\hat{\underline{l}}_{kN}}{r_{kN}^3}\right|\underline{H}_0\cdot\underline{\psi}_1\right\rangle$$

$$-\frac{1}{N}\sum_{n\neq N}\frac{2Z_n}{M_nc}\left\langle\psi_0\left|\underline{\mu}_N\cdot\frac{\hat{\underline{l}}_{nN}}{r_{nN}^3}\right|\underline{H}_0\cdot\underline{\psi}_1\right\rangle \tag{1.10}$$

Now, expressing $\underline{r}_{ko}=\underline{r}_{kN}+\underline{R}_{No}$ where $\underline{R}_{No}$ is the vector from the origin of the vector potential to the nucleus 'N', and noting that

$$(\underline{A}\times\underline{B})\cdot(\underline{C}\times\underline{D})=(\underline{A}\cdot\underline{C})(\underline{B}\cdot\underline{D})-(\underline{A}\cdot\underline{D})(\underline{B}\cdot\underline{C})$$

we have from eqs. 1.4 and 1.10

$$\underline{\mu}_N\cdot\underline{\underline{\sigma}}_N\cdot\underline{H}_0=\sum_{\nu,\lambda}(\underline{\mu}_N)_\nu\,\sigma_{\nu\lambda}(\underline{H}_0)_\lambda$$

$$=\frac{1}{N}\sum_{k}\frac{e^2}{2mc^2}\left[\left\langle\psi_0\left|\frac{(\underline{H}_0\cdot\underline{\mu}_N)\,r_{kN}^2-(\underline{H}_0\cdot\underline{r}_{kN})(\underline{\mu}_N\cdot\underline{r}_{kN})}{r_{kN}^3}\right|\psi_0\right\rangle\right.$$

$$\left.+\left\langle\psi_0\left|\frac{(\underline{H}_0\cdot\underline{\mu}_N)(\underline{r}_{kN}\cdot\underline{R}_{No})-(\underline{H}_0\cdot\underline{r}_{kN})(\underline{\mu}_N\cdot\underline{R}_{No})}{r_{kN}^3}\right|\psi_0\right\rangle\right]$$

$$+\frac{1}{N}\sum_{n\neq N}\frac{Z_n^2}{2M_nc^2}\left[\left\langle\psi_0\left|\frac{(\underline{H}_0\cdot\underline{\mu}_N)\,r_{nN}^2-(\underline{H}_0\cdot\underline{r}_{nN})(\underline{\mu}_N\cdot\underline{r}_{nN})}{r_{nN}^3}\right|\psi_0\right\rangle\right.$$

$$\left.+\left\langle\psi_0\left|\frac{(\underline{H}_0\cdot\underline{\mu}_N)(\underline{r}_{nN}\cdot\underline{R}_{No})-(\underline{H}_0\cdot\underline{r}_{nN})(\underline{\mu}_N\cdot\underline{R}_{No})}{r_{nN}^3}\right|\psi_0\right\rangle\right]$$

$$-\frac{1}{N}\sum_{n\neq N}\frac{2Z_n}{M_nc}\left\langle\psi_0\left|\frac{\underline{\mu}_N\cdot\hat{\underline{l}}_{nN}}{r_{nN}^3}\right|\underline{H}_0\cdot\underline{\psi}_1\right\rangle \tag{1.11}$$

$$-\frac{1}{N}\sum_{k}\frac{2e}{mc}\left\langle\psi_0\left|\frac{\underline{\mu}_N\cdot\hat{\underline{l}}_{kN}}{r_{kN}^3}\right|\underline{H}_0\cdot\underline{\psi}_1\right\rangle$$

Examination of eq. 1.7 shows that $\mathcal{N}$ is equal to one to first order in $\underline{H}_o$ since

$$\langle \underline{H}_o \cdot \underline{\psi}_1 | \psi_o \rangle = \langle \psi_o | \underline{H}_o \cdot \underline{\psi}_1 \rangle$$

hence

$$\mathcal{N} = 1 + \langle \underline{H}_o \cdot \underline{\psi}_1 | \underline{H}_o \cdot \underline{\psi}_1 \rangle + \cdots$$

since

$$\frac{1}{\mathcal{N}} = 1 - \langle \underline{H}_o \cdot \underline{\psi}_1 | \underline{H}_o \cdot \underline{\psi}_1 \rangle + \cdots$$

we will henceforth drop the normalization constant.

By the arguments of Chan and Das[4] we notice that the Hamiltonian for the molecule in the presence of external fields is not gauge invariant due to the $\underline{H}_o \times \underline{r}_{ko}$ term, hence $\underline{\psi}_1$ is not gauge invariant. However, the expression for the shielding must be gauge invariant if it is to correspond to an observable. Notice that the first and third terms of eq. 1.11 are gauge invariant to first order in $\underline{H}_o$ because ψ_o is gauge invariant. Then the sum of the remaining terms must be gauge invariant. In principle, the dependence of the shielding energy on perturbation terms may be eliminated by a proper choice of gauge for the vector potential. Kern and Lipscomb[7][8] have proposed an 'average energy' approximation for the choice of origin which they have applied to several diatomic molecules with better results for heteronuclear molecules than for homonuclear ones such as H_2. Chan and Das have proposed the electronic centroid as origin because the paramagnetic part of the susceptability is a minimum with this choice of gauge. We will return to this problem after developing the familiar expressions for the shielding.

If we choose a set of Cartesian basis vectors we may write

$$\underline{\mu}_N \cdot \underset{\sim}{\sigma}_N \cdot \underline{H}_0 = \sum_{\nu,\lambda} (\underline{\mu}_N)_\nu \, \sigma_{\nu\lambda} \, (\underline{H}_0)_\lambda \qquad (1.12)$$

We note that

$$(\underline{A}\cdot\underline{B})(\underline{C}\cdot\underline{D}) = \sum_\nu A_\nu B_\nu (\underline{C}\cdot\underline{D}) = \sum_{\nu,\lambda} A_\nu B_\lambda (\underline{C}\cdot\underline{D})\, \delta_{\nu\lambda}$$

$$= \sum_{\nu,\lambda} A_\nu B_\nu C_\lambda D_\lambda \qquad \delta_{\nu\lambda} = \begin{cases} 0 \,; & \nu \neq \lambda \\ 1 \,; & \nu = \lambda \end{cases}$$

for any vectors $\underline{A}$, $\underline{B}$, $\underline{C}$, $\underline{D}$.

Hence we may write eq. 1.11 as

$$\sum_{\nu,\lambda} (\underline{\mu}_N)_\nu \, \sigma_{\nu\lambda} (\underline{H}_0)_\lambda = \sum_{\nu,\lambda} \Bigg[\sum_k \frac{e^2}{2mc^2} \Bigg(\Big\langle \psi_0 \Big| \frac{(\underline{H}_0)_\lambda (\underline{\mu}_N)_\nu r_{kN}^2 \delta_{\nu\lambda} - (\underline{H}_0)_\lambda (\underline{r}_{kN})_\lambda (\underline{r}_{kN})_\nu (\underline{\mu}_N)_\nu}{r_{kN}^3} \Big| \psi_0 \Big\rangle$$

$$+ \Big\langle \psi_0 \Big| \frac{(\underline{H}_0)_\lambda (\underline{\mu}_N)_\nu (\underline{r}_{kN}\cdot\underline{R}_{N0}) \delta_{\nu\lambda} - (\underline{H}_0)_\lambda (\underline{r}_{kN})_\lambda (\underline{\mu}_N)_\nu (\underline{R}_{N0})_\nu}{r_{kN}^3} \Big| \psi_0 \Big\rangle \Bigg)$$

$$- \frac{2e}{mc} \sum_k \Big\langle \psi_0 \Big| \frac{(\underline{\mu}_N)_\nu (\hat{\underline{\ell}}_{kN})_\nu}{r_{kN}^3} \Big| (\underline{H}_0)_\lambda \, \psi_{1\lambda} \Big\rangle \qquad (1.13)$$

where the nuclear terms have been dropped since, in general,

$$\frac{Z_n/M_n}{-e/m_e} < 5.5 \times 10^{-4}$$

Equating terms in $(\underline{H}_0)_\lambda$, $(\underline{\mu}_N)_\nu$ from eq. 1.13, we find

$$\sigma_{\nu\lambda} = \frac{e^2}{2mc^2} \sum_k \Bigg[\Big\langle \psi_0 \Big| \frac{r_{kN}^2 \delta_{\nu\lambda} - (\underline{r}_{kN})_\nu (\underline{r}_{kN})_\lambda}{r_{kN}^3} \Big| \psi_0 \Big\rangle$$

$$+ \Big\langle \psi_0 \Big| \frac{(\underline{r}_{kN}\cdot\underline{R}_{N0})\, \delta_{\nu\lambda} - (\underline{R}_{N0})_\nu (\underline{r}_{kN})_\lambda}{r_{kN}^3} \Big| \psi_0 \Big\rangle \Bigg]$$

$$- \frac{2e}{mc} \sum_k \Big\langle \psi_0 \Big| \frac{(\hat{\underline{\ell}}_{kN})_\nu}{r_{kN}^3} \Big| \psi_{1\lambda} \Big\rangle \qquad (1.14)$$

It is now convenient to express $\underset{\sim}{\sigma}$ as the sum of three terms

$$\underset{\sim}{\sigma} = \underset{\sim}{\sigma}^{d} + \underset{\sim}{\sigma}_{G}^{P} + \underset{\sim}{\sigma}_{EX}^{P}$$

where

$$(\underset{\sim}{\sigma}^{d})_{\nu\lambda} = \frac{e^2}{2mc^2}\sum_{k}\left\langle\psi_0\left|\frac{r_{kN}^2\,\delta_{\nu\lambda} - (r_{kN})_\nu(r_{kN})_\lambda}{r_{kN}^3}\right|\psi_0\right\rangle$$

$$(\underset{\sim}{\sigma}_{G}^{P})_{\nu\lambda} = \frac{e^2}{2mc^2}\sum_{k}\left\langle\psi_0\left|\frac{(r_{kN}\cdot R_{NO})\,\delta_{\nu\lambda} - (R_{NO})_\nu(r_{kN})_\lambda}{r_{kN}^3}\right|\psi_0\right\rangle$$

$$(\underset{\sim}{\sigma}_{EX}^{P})_{\nu\lambda} = \frac{-2e}{mc}\sum_{k}\left\langle\psi_0\left|\frac{(\hat{l}_{kN})_\nu}{r_{kN}^3}\right|\psi_{1\lambda}\right\rangle \tag{1.15}$$

Here $\underset{\sim}{\sigma}^{d}$ is the Lamb term and $\underset{\sim}{\sigma}_{G}^{P}+\underset{\sim}{\sigma}_{EX}^{P}$ is the equivalent of the paramagnetic term introduced by Ramsey. The fact that $(\underset{\sim}{\sigma}_{G}^{P})_{\nu\lambda}$ is negative may be hidden by the use of R_{NO} in the expression rather than R_{ON}.

Experimentally, when a molecule is undergoing rapid, random tumbling, as in the gas phase, one measures only the isotropic part of $\underset{\sim}{\sigma}$ represented by the scalar

$$\sigma_{AVG} = \sigma_{AVG}^{d} + \sigma_{G\,AVG}^{P} + \sigma_{EX\,AVG}^{P} \tag{1.16}$$

where

$$\sigma_{AVG}^{d} = \frac{\sigma_{xx}^{d} + \sigma_{yy}^{d} + \sigma_{zz}^{d}}{3}$$

Similar expressions are obtained for $\sigma_{G\,AVG}^{P}$ and $\sigma_{EX\,AVG}^{P}$. 'x', 'y', and 'z' represent a set of Cartesian basis vectors fixed in the molecule. Performing the averages we obtain for the diamagnetic term

$$\sigma^{d}_{AVG} = \frac{e^2}{6mc^2}\sum_{K}\left\langle \psi_0 \left| \frac{3r_{KN}^2 - (r_{KN})_x^2 - (r_{KN})_y^2 - (r_{KN})_z^2}{r_{KN}^3} \right| \psi_0 \right\rangle$$

$$= \frac{e^2}{3mc^2}\sum_{K}\left\langle \psi_0 \left| \frac{1}{r_{KN}} \right| \psi_0 \right\rangle \qquad (1.17)$$

For the ground state term of the paramagnetic part we find

$$\sigma^{P}_{GAVG} = \frac{e^2}{3mc^2}\sum_{K}\left\langle \psi_0 \left| \frac{(R_{NO})_x (r_{KN})_x + (R_{NO})_y (R_{KN})_y + (R_{NO})_z (r_{KN})_z}{r_{KN}^3} \right| \psi_0 \right\rangle \qquad (1.18)$$

At this point it is convenient to make the Born-Oppenheimer approximation[9] and write

$$\psi_0 = \psi_n \psi_e \qquad (1.19)$$

where (see eq. 1.1)

$$\hat{\mathcal{H}}_{electronic}\,\psi_e = E_e \psi_e \qquad (1.20)$$

for fixed internuclear distances, and ψ_n is a solution of

$$\left[\hat{\mathcal{H}}_{nuclear} + E_e(R)\right]\psi_n = E_{TOTAL}\,\psi_n \qquad (1.21)$$

Here $E_e(R)$ denotes the fact that E_e is a function of nuclear coordinates. We may now write, for any operator $\hat{O}$ corresponding to the observable $\langle O \rangle$

$$\langle O \rangle = \langle \psi_0 | \hat{O} | \psi_0 \rangle_{V_T}$$

$$= \left\langle \psi_n \middle| \langle \psi_e | \hat{O} | \psi_e \rangle_{V_e} \middle| \psi_n \right\rangle_{V_n} \qquad (1.22)$$

where V_e and V_n refer to integration over electronic and nuclear configuration spaces respectively. In general ψ_e (and $\hat{O}$) are explicit or implicit functions of nuclear coordinates, hence we write

$$\langle O \rangle = \langle \psi_n | \hat{O}(R) | \psi_n \rangle_{V_n} \tag{1.23}$$

where

$$\hat{O}(R) = \langle \psi_e | \hat{o} | \psi_e \rangle_{V_e}$$

We may now rewrite eqs. 1.17 and 1.18 as

$$\sigma^{d}_{AVG} = \frac{e^2}{3mc^2} \sum_k \langle \psi_n | \langle \psi_e | \frac{1}{r_{kN}} | \psi_e \rangle_{V_e} | \psi_n \rangle_{V_n} \tag{1.24}$$

$$\sigma^{p}_{G\,AVG} = \frac{e^2}{3mc^2} \sum_k \langle \psi_n | \underline{R}_{NO} \cdot \langle \psi_e | \frac{\underline{r}_{kN}}{r_{kN}^3} | \psi_e \rangle_{V_e} | \psi_n \rangle_{V_n} \tag{1.25}$$

We now examine the total force on the nucleus 'N' which we write in terms of a potential V. In the unperturbed system the forces are electrostatic and we have the vector equation

$$\underline{F}_N = -\nabla_N V = Z_N \left[\sum_{n \neq N} \frac{Z_n \underline{r}_{Nn}}{r_{Nn}^3} + |e| \sum_k \langle \psi_e | \frac{\underline{r}_{kN}}{r_{kN}^3} | \psi_e \rangle_{V_e} \right] \tag{1.26}$$

or, upon rearranging,

$$e \sum \langle \psi_e | \frac{\underline{r}_{kN}}{r_{kN}^3} | \psi_e \rangle_{V_e} = \sum_{n \neq N} \frac{Z_n \underline{r}_{Nn}}{r_{Nn}} + \frac{1}{Z_N} \nabla_N V \tag{1.27}$$

But V is just the potential part of the Hamiltonian in eq. 1.21

$$V = \sum_{N<N'} \frac{Z_N Z_{N'}}{r_{NN'}} + E_e(R) \tag{1.28}$$

Then

$$\nabla_N V = -\sum_{n \neq N} \frac{Z_N Z_n \underline{r}_{Nn}}{r_{Nn}^3} + \nabla_N E_e(R) \tag{1.29}$$

or, from eq. 1.27,

$$e \sum_{k} \left\langle \psi_e \left| \frac{\underline{r}_{kN}}{r_{kN}^3} \right| \psi_e \right\rangle_{V_e} = \nabla_N E_e(R) \tag{1.30}$$

Hence the electronic integrals may be eliminated from eq. 1.25 yielding the 'vector' equation

$$\sigma^P_{G\,AVG} = \frac{e}{3mc^2} \left\langle \psi_n \right| \underline{R}_{NO} \cdot \nabla_N E_e(R) \left| \psi_n \right\rangle_{V_n} \tag{1.31a}$$

Note that $\sigma^P_{G\,AVG}$ is quite sensitive to the behavior of $E_e(R)$ as a function of internuclear separations. In practice it is convenient to use the equivalent expression[11]

$$\sigma^P_{G\,AVG} = \frac{e}{3mc^2} \left\langle \psi_n \right| \underline{R}_{NO} \cdot \left[\sum_{n \neq N} \frac{Z_n \underline{r}_{Nn}}{r_{Nn}^3} + \frac{1}{Z_N} \nabla_N V \right] \left| \psi_n \right\rangle_{V_n} \tag{1.31b}$$

since accurate empirical potential functions are available over a wide range of nuclear separations.[14]

The excited state term may be estimated by use of a variation calculation. Das and Bersohn[10] have shown that for many H_2 wave functions a one-parameter calculation is sufficient to estimate the excited state contribution. Chan and co-workers[3] have performed a variational calculation for H_2 using the zero-order functions of Kolos and Roothaan. The function used was of the form

$$\psi_{pert} = (1 + ia\, \underline{H}_0 \cdot \underline{P})\, \psi_0 \tag{1.32}$$

where

$$P_x = yz$$
$$P_y = xz$$
$$P_z = 0$$

The bond axis is the 'z' axis and the origin is at the electronic centroid. Then $(\sigma_{EX}^{P})_{\perp} = (\sigma_{EX}^{P})_{xx} = (\sigma_{EX}^{P})_{yy}$ is given by[11]

$$(\sigma_{EX}^{P})_{\perp} = \frac{-e^2}{2mc^2}\left\{\left\langle\psi_0\left|\sum_k \frac{z_{kN}^2 - x_{kN}^2}{r_{kN}^2}\right|\psi_0\right\rangle - \left\langle\psi_0\left|\left|R_{N0}\right|\sum_k \frac{z_{kN}}{r_{kN}^3}\right|\psi_0\right\rangle\right\}$$

$$\times \frac{\left\langle\psi_0\left|\sum_k z_{k0}^2 - x_{k0}^2\right|\psi_0\right\rangle}{\left\langle\psi_0\left|\sum_k z_{k0}^2 + x_{k0}^2\right|\psi_0\right\rangle} \qquad (1.33)$$

with the above choice of origin.

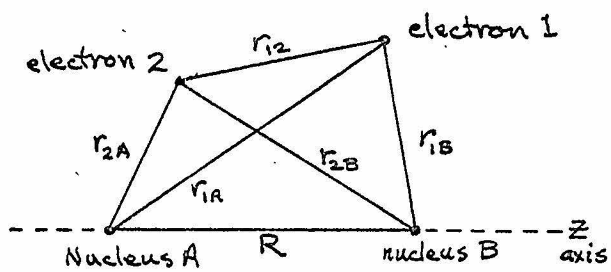
III - Matrix elements of the diamagnetic shielding

Kolos and Roothaan's electronic wave functions for the ${}^1\Sigma_g^+$ ground state of H_2 are of the form[1]

$$\Psi_e = \sum_i c_i \Phi_i \qquad \text{where} \qquad \Phi_i = \psi_{p_i q_i r_i s_i \mu_i} + \psi_{r_i s_i p_i q_i \mu_i} \qquad (2.1)$$

$$\text{and} \qquad \psi_{pqrs\mu} = e^{-\alpha(\xi_1+\xi_2)}\, \xi_1^{\,p} \eta_1^{\,q} \xi_2^{\,r} \eta_2^{\,s} r_{12}^{\,\mu}$$

'p', 'q', 'r', 's', and 'μ' are non-negative integers, and α and the c_i are real. ξ_i and η_i are the elliptic coordinates defined by[12]



$$\xi_i = \frac{r_{iA}+r_{iB}}{R} \qquad \eta_i = \frac{r_{iA}-r_{iB}}{R}$$

$\varphi_1 - \varphi_2$ = angular separation of electrons about z, or bond, axis

$$dV_i = \frac{R^3}{8}\left(\xi_i^2 - \eta_i^2\right) d\xi_i\, d\eta_i\, d\varphi_i \qquad (2.1^*)$$

For any electronic operator $\hat{O}$ we may calculate the expectation value at internuclear distance R as follows (see eq. 1.23)

$$\hat{O}(R) = \langle \Psi_e | \hat{O} | \Psi_e \rangle \qquad \left\langle \sum_i c_i \Phi_i \middle| \hat{O} \middle| \sum_j c_j \Phi_j \right\rangle$$

$$= \sum_{i,j} c_i c_j \langle \hat{O} \rangle_{ij} \qquad ; \langle \hat{O} \rangle_{ij} \quad \langle \Phi_i | \hat{O} | \Phi_j \rangle \qquad (2.2)$$

since the c_i are real.

In the case that $\hat{O}$ is the sum of one-electron operators, $\hat{O} = \sum_k \hat{O}_k$ we may write

$$\langle \hat{O} \rangle_{ij} = \left\langle \Phi_i \middle| \sum_k \hat{O}_k \middle| \Phi_j \right\rangle = \sum_k \langle \hat{O}_k \rangle_{ij} \qquad (2.3)$$

It is now worthwhile to note that Kolos and Roothaan's ${}^1\Sigma_g^+$ molecular orbital is symetric with respect to electron exchange. Furthermore it must be symetric with respect to interchange of nuclei which requires $q+s$ even in each $\psi_{pqrs\mu}$. Since neither the mass or spin of the nuclei enter the calculation of the electronic wave functions, the MO is equally applicable to H_2, HD, and D_2.

Now if $\hat{O}$ is the sum of 'identical' one-electron operators, that is, symetric with respect to exchange of electrons, then

$$\langle \hat{O} \rangle_{ij} = \sum_k \langle \Phi_i | \hat{O}_k | \Phi_j \rangle = N_e \langle \Phi_i | \hat{O}_k | \Phi_j \rangle = N_e \langle \hat{O}_k \rangle_{ij} \qquad (2.4)$$

where N_e is the number of electrons in the molecule described by ψ_e, and 'k' now refers to a particular, but arbitrarily chosen, electron. We can now expand eq. 2.4 to obtain

$$\langle \hat{O} \rangle_{ij} = N_e \Big[\langle p_i q_i r_i s_i \mu_i | \hat{O}_k | p_j q_j r_j s_j \mu_j \rangle + \langle p_i q_i r_i s_i \mu_i | \hat{O}_k | r_j s_j p_j q_j \mu_j \rangle$$

$$+ \langle r_i s_i p_i q_i \mu_i | \hat{O}_k | p_j q_j r_j s_j \mu_j \rangle + \langle r_i s_i p_i q_i \mu_i | \hat{O}_k | r_j s_j p_j q_j \mu_j \rangle \qquad (2.5)$$

where $\langle p_i q_i r_i s_i \mu_i | \hat{O}_k | p_j q_j r_j s_j \mu_j \rangle$ is obviously $\langle \psi_{p_i q_i r_i s_i \mu_i} | \hat{O}_k | \psi_{p_j q_j r_j s_j \mu_j} \rangle$ and the physics demands $N_e = 2$, $k = 1 \text{ or } 2$.

We will now consider the integrals $\langle p_i q_i r_i s_i \mu_i | \hat{O}_k | p_j q_j r_j s_j \mu_j \rangle$ where $\hat{O}_k = \frac{1}{r_{1A}}$ since the Lamb term may be expressed in terms of these integrals by use of the above expressions. The reduction follows the procedure outlined by Kolos and Roothaan.[13]

$$\frac{1}{r_{1A}} = \frac{2}{R(\xi_1+\eta_1)} = \frac{2(\xi_1-\eta_1)}{R(\xi_1^2-\eta_1^2)} \qquad (\text{see eq. } 2.1*)$$

Then

$$\left\langle pqrs\mu \right| \frac{1}{r_{1A}} \left| p'q'r's'\mu' \right\rangle = \frac{2}{R} \iint_{\text{all space}} dV_1 dV_2\, e^{-2\alpha(\xi_1+\xi_2)} \xi_1^{\bar{p}} \eta_1^{\bar{q}} \xi_2^{\bar{r}} \eta_2^{\bar{s}} r_{12}^{\bar{\mu}} (\xi_1-\eta_1)(\xi_1^2-\eta_1^2)^{-1}$$

$$\bar{p} = p+p';\ \bar{q} = q+q';\ \text{etc.}$$

$$= \frac{2}{R}\left[K_{\bar{p}+1,\bar{q},\bar{r},\bar{s},}{}^{\bar{\mu}} - K_{\bar{p},\bar{q}+1,\bar{r},\bar{s}}{}^{\bar{\mu}}\right] \qquad (2.6)$$

where

$$K_{p,q,r,s,}{}^{\mu} = \iint_{\text{all space}} dV_1 dV_2\, e^{-2\alpha(\xi_1+\xi_2)} (\xi_1^2-\eta_1^2)^{-1} \xi_1^{p} \eta_1^{q} \xi_2^{r} \eta_2^{s} r_{12}^{\mu} \qquad (2.7)$$

In order to reduce eq. 2.7 we define the following one-electron functions. Our notation is slightly different from that of Kolos and Roothaan[13] for reasons of generality. We also note Kolos and Roothaan's notation to facilitate comparison with reference 13.

<u>Our notation</u>	<u>Kolos and Roothaan's</u>
$\Sigma_{1pq} = e^{-2\alpha\xi}\xi^p\eta^q$	Σ_1
$\Sigma_2 = (\xi^2+\eta^2-1)\Sigma_1$	Σ_2
$\Sigma_3 = (\xi^2+\eta^2-1)^2\Sigma_1$	Σ_3
$\Sigma_4 = \xi^2\eta^2\Sigma_1$	Σ_5
$\Sigma_5 = (\xi^2-1)(1-\eta^2)\Sigma_1$	Σ_7

$$\Sigma_6 = \xi\eta\,\Sigma_1$$

Σ_4

$$\Sigma_7 = \xi\eta\left(\xi^2+\eta^2-1\right)\Sigma_1$$

Σ_6

$$\Pi_n = \left[(\xi^2-1)(1-\eta^2)\right]^{\frac{1}{2}}\cos\varphi\,\Sigma_n$$

Π_1, Π_2 same as ours
their Π_3 = our Π_6

$$\Delta_n = (\xi^2-1)(1-\eta^2)\cos 2\varphi\,\Sigma_n$$

defines only Δ_1

$$\Sigma_n^* = (\xi^2-\eta^2)\,\Sigma_n$$

$$\Pi_n^* = (\xi^2-\eta^2)\,\Pi_n$$

$$\Delta_n^* = (\xi^2-\eta^2)\,\Delta_n \qquad (2.8)$$

same definitions
note above differences

The K integrals, eq. 2.7, may now be expressed in terms of the following integrals and notation

$$\langle\psi|\Omega^*\rangle = \iint dV_1 dV_2\,(\xi_1^2-\eta_1^2)^{-1}(\xi_2^2-\eta_2^2)^{-1}\psi(1)\,\Omega^*(2) \qquad (2.9)$$

$$[\psi|\Omega^*] = \iint dV_1 dV_2\,(\xi_1^2-\eta_1^2)^{-1}(\xi_2^2-\eta_2^2)^{-1}\psi(1)\,\Omega^*(2)\;r_{12}^{-1} \qquad (2.10)$$

where ψ, Ω represent any of the functions of eqs. 2.8. We will make use of the relation[13]

$$r_{12}^2 = \frac{R^2}{4}\Big\{\xi_1^2+\eta_1^2+\xi_2^2+\eta_2^2-2\xi_1\eta_1\xi_2\eta_2-2$$
$$-2\left[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}\cos(\varphi_1-\varphi_2)\Big\} \qquad (2.11)$$

For Kolos and Roothaan's wave functions the values of $\bar{\mu}$ of interest in eq. 2.6 are $0 \leq \bar{\mu} \leq 4$. The integrals with $\bar{\mu}$ even are easier and will be treated first.

$$K_{pqrs}{}^{0} = \iint dV_1 dV_2 (\xi_1^2 - \eta_1^2)^{-1} e^{-2\alpha(\xi_1+\xi_2)} \xi_1^p \eta_1^q \xi_2^r \eta_2^s$$

$$= \iint dV_1 dV_2 (\xi_1^2-\eta_1^2)^{-1} (\xi_2^2-\eta_2^2)^{-1} (\xi_2^2-\eta_2^2) e^{-2\alpha\xi_1} \xi_1^p \eta_1^q e^{-2\alpha\xi_2} \xi_2^r \eta_2^s$$

$$= \langle \Sigma_{1pq} | \Sigma^*_{1rs} \rangle \qquad (2.12)$$

The p,q,r,s indices will be suppressed and the equations written in the form $K^0 = \langle \Sigma_1 | \Sigma_1^* \rangle$. We now rewrite eq. 2.11 as

$$r_{12}^2 = \frac{R^2}{4} \Big\{ (\xi_1^2+\eta_1^2-1) + (\xi_2^2+\eta_2^2-1) - 2\xi_1\eta_1\xi_2\eta_2$$

$$- 2\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}} \left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}} \cos\varphi_1 \cos\varphi_2$$

$$-2\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}} \left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}} \sin\varphi_1 \sin\varphi_2 \Big\} \qquad (2.11^*)$$

Inserting into eq. 2.7 yields immediately

$$K^2 = \frac{R^2}{4}\left[\langle \Sigma_2 | \Sigma_1^* \rangle + \langle \Sigma_2 | \Sigma_1^* \rangle - 2 \langle \Sigma_6 | \Sigma_6^* \rangle \right] \qquad (2.13)$$

where we observe that $\langle \psi | \Omega^* \rangle = 0$ when either ψ or Ω^* are π, Δ functions since the angular parts factor and

$$\int_a^{2\pi+a} \cos\varphi \, d\varphi = \int_a^{2\pi+a} \sin\varphi \, d\varphi = \int_a^{2\pi+a} \cos 2\varphi \, d\varphi = \int_a^{2\pi+a} \sin 2\varphi \, d\varphi = 0 \qquad (2.14)$$

We use eq 2.11* to obtain

$$r_{12}^4 = \frac{R^4}{16}\Big\{ (\xi_1^2+\eta_1^2-1)^2 + (\xi_2^2+\eta_2^2-1)^2 + 4\xi_1^2\eta_1^2\xi_2^2\eta_2^2 - 4\xi_1\eta_1\xi_2\eta_2(\xi_2^2+\eta_2^2-1)$$

$$+2(\xi_1^2+\eta_1^2-1)(\xi_2^2+\eta_2^2-1) - 4(\xi_1^2+\eta_1^2-1)\xi_1\eta_1\xi_2\eta_2$$

$$+4\left[(\xi_1^2-1)(1-\eta_1^2)\right]\left[(\xi_2^2-1)(1-\eta_2^2)\right]\cos^2\varphi_1\cos^2\varphi_2$$

$$+4\left[(\xi_1^2-1)(1-\eta_1^2)\right]\left[(\xi_2^2-1)(1-\eta_2^2)\right]\sin^2\varphi_1\sin^2\varphi_2$$

$$-4(\xi_1^2+\eta_1^2-1)\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}}\left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}\cos\varphi_1\cos\varphi_2$$

$$-4(\xi_1^2+\eta_1^2-1)\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}}\left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}\sin\varphi_1\sin\varphi_2$$

$$-4\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}}\left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}(\xi_2^2+\eta_2^2-1)\cos\varphi_1\cos\varphi_2$$

$$-4\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}}\left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}(\xi_2^2+\eta_2^2-1)\sin\varphi_1\sin\varphi_2$$

$$+8\xi_1\eta_1\xi_2\eta_2\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}}\left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}\cos\varphi_1\cos\varphi_2$$

$$+8\xi_1\eta_1\xi_2\eta_2\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}}\left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}}\sin\varphi_1\sin\varphi_2$$

$$+2\left[(\xi_1^2-1)(1-\eta_1^2)\right]\left[(\xi_2^2-1)(1-\eta_2^2)\right]\sin 2\varphi_1\sin 2\varphi_2 \Big\} \qquad (2.15)$$

We use the relations

$$\int_a^{2\pi+a}\sin^2\varphi\,d\varphi = \int_a^{2\pi+a}\cos^2\varphi\,d\varphi = \pi = \frac{1}{2}\int_a^{2\pi+a}d\varphi \qquad (2.16)$$

and substitute eq. 2.15 into eq. 2.7 to find

$$K^4 = \frac{R^4}{16}\Big[\langle\Sigma_3|\Sigma_1^*\rangle + \langle\Sigma_1|\Sigma_3^*\rangle + 4\langle\Sigma_4|\Sigma_4^*\rangle$$

$$+2\langle\Sigma_5|\Sigma_5^*\rangle+2\langle\Sigma_2|\Sigma_2^*\rangle-4\langle\Sigma_7|\Sigma_6^*\rangle$$

$$-4\langle\Sigma_6|\Sigma_7^*\rangle \qquad (2.17)$$

For $\bar{\mu}$ odd the process is slightly more complicated except for $\bar{\mu}=-1$ where it is obvious from eqs. 2.7-9 that

$$K^{-1}=[\Sigma_1|\Sigma_1^*] \qquad (2.18)$$

At this point we rewrite eq. 2.7 as

$$K^{\mu}=\iint dV_1 dV_2\, e^{-2\alpha(\xi_1+\xi_2)}(\xi_1^2-\eta_1^2)^{-1}\xi_1^p\eta_1^q\xi_2^r\eta_2^s\,\frac{r_{12}^{\bar{\mu}+1}}{r_{12}} \qquad (2.7^*)$$

and use eqs. 2.11* and 2.15 and the Von Neumann expansion for r_{12}^{-1} (15):

$$\frac{1}{r_{12}}=\frac{2}{R}\sum_{L=0}^{\infty}\sum_{i=0}^{L}D_{Li}\,Q_L^i(\xi_>)P_L^i(\xi_<)P_L^i(\eta_1)P_L^i(\eta_2)\cos i(\varphi_1-\varphi_2) \qquad (2.19)$$

where

$$D_{Li}=\begin{cases}2L+1 & ;\ i=0\\ (-1)^i\,2(2L+1)\left[\dfrac{(L-i)!}{(L+i)!}\right]^2 & i\geq 1\end{cases}$$

$\xi_>$ is the larger of ξ_1 and ξ_2, $\xi_<$ is the smaller. Q_L^i and P_L^i are the associated Legendre functions. Of immediate interest is the angular part of the expansion:

$$\cos i(\varphi_1-\varphi_2)=\cos i\varphi_1\cos i\varphi_2+\sin i\varphi_1\sin i\varphi_2$$

We note that

$$\int_0^{2\pi}\sin m\varphi\cos n\varphi\,d\varphi=0 \quad \text{for all integers } m \text{ and } n$$

$$\int_0^{2\pi} \sin m\varphi \sin n\varphi \, d\varphi = \int_0^{2\pi} \cos m\varphi \cos n\varphi \, d\varphi = \begin{cases} 0 \; ; & m \neq n \\ \pi & m = n \neq 0 \end{cases} \tag{2.20}$$

Hence the terms in the K integrals involving sin-cos products will disappear upon integration and the $\sin i\varphi \sin \varphi$ parts may be replaced by $\cos i\varphi \cos \varphi$. This is equivalent to a transformation of φ by $\frac{\pi}{2}$ in the appropriate integrals and the use of orthogonality. For $\bar{\mu}=1$ we have, from eqs. 2.7*and 2.11*,

$$K' = \frac{R^2}{4} \iint dV_1 dV_2 \, (\xi_1^2 - \eta_1^2)^{-1} (\xi_2^2 - \eta_2^2)^{-1} (\xi_2^2 - \eta_2^2) e^{-2\alpha(\xi_1+\xi_2)} \xi_1^p \eta_1^q \xi_2^r \eta_2^s \, r_{12}^{-1}$$

$$\times \Big\{ (\xi_1^2 + \eta_1^2 - 1) + (\xi_2^2 + \eta_2^2 - 1) - 2\xi_1\eta_1\xi_2\eta_2$$

$$- 2\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}} \left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}} \cos\varphi_1 \cos\varphi_2$$

$$- 2\left[(\xi_1^2-1)(1-\eta_1^2)\right]^{\frac{1}{2}} \left[(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{1}{2}} \sin\varphi_1 \sin\varphi_2 \Big\} \tag{2.21}$$

Using eqs. 2.8, 2.10, and 2.20, this may be written as

$$K' = \frac{R^2}{4} \left([\Sigma_2 | \Sigma_1^*] + [\Sigma_1 | \Sigma_2^*] - 2 [\Sigma_6 | \Sigma_6^*] - 4 [\pi_1 | \pi_1^*] \right) \tag{2.22}$$

For $\mu=3$ the reduction becomes very involved. In spirit, we rewrite the terms of eq. 2.15 involving $\sin^2\varphi$ and $\cos^2\varphi$ using the relations

$$\sin^2\varphi = \frac{1}{2}(1-\cos 2\varphi) \quad ; \quad \cos^2\varphi = \frac{1}{2}(1+\cos 2\varphi)$$

or $$\cos^2\varphi_1 \cos^2\varphi_2 + \sin^2\varphi_1 \sin^2\varphi_2 = \frac{1}{4}(1 + 2\cos 2\varphi_1 \cos 2\varphi_2) \tag{2.23}$$

Then eq. 2.23 combined with eq. 2.15 and substituted into eq. 2.7* may be reduced using eqs. 2.20 and 2.10 to the form

$$K^3 = \frac{R^4}{16}\Big([\Sigma_1|\Sigma_3^*] + [\Sigma_3|\Sigma_1^*] + 4[\Sigma_4|\Sigma_4^*] + 4[\Delta_1|\Delta_1^*] + 2[\Sigma_5|\Sigma_5^*] + 2[\Sigma_2|\Sigma_2^*] - 4[\Sigma_7|\Sigma_6^*] - 8[\Pi_2|\Pi_1^*] - 4[\Sigma_6|\Sigma_7^*] - 8[\Pi_1|\Pi_2^*] + 16[\Pi_6|\Pi_6^*]\Big) \qquad (2.24)$$

We may now proceed with the reduction of eqs. 2.9 and 2.10 by expressing the charge distributions in general as

$$\varphi^M_{kpq} = e^{-2\alpha\xi} \sum_{a,b} \delta_{kab}\, \xi^{p+a} \eta^{q+b} \left[(\xi^2-1)(1-\eta^2)\right]^{\frac{M}{2}} \cos M\varphi \qquad (2.25)$$

where the φ^m_{kpq} represent the Σ_k, Π_k, Δ_k, functions for $M = 0, 1, 2$ respectively, and the δ_{kab} are the coefficients as determined from the eqs. 2.8. We also define φ^{m*}_{kpq} in the same manner as eq. 2.25 with coefficients δ^*_{kab}. The δ_k and δ^*_k are tabulated in Appendix 1.

The righthand side of eq. 2.9 vanishes for $M > 0$ (see eq. 2.14) so we consider the case $M=0$.

$$\langle \varphi^0_{kpq} | \varphi^{0*}_{lrs} \rangle = \iint dV_1 dV_2 (\xi_1^2-\eta_1^2)^{-1} (\xi_2^2-\eta_2^2)^{-1} e^{-2\alpha(\xi_1+\xi_2)} \times \Big(\sum_{a,b} \delta_{kab}\, \xi_1^{p+a} \eta_1^{q+b}\Big)\Big(\sum_{c,d} \delta^*_{lcd}\, \xi_2^{r+c} \eta_2^{s+d}\Big)$$

$$= \frac{R^6}{64}(2\pi)^2 \left[\sum_{a,b} \delta_{kab} \int_1^\infty d\xi_1 e^{-2\alpha\xi_1} \xi_1^{p+a} \int_{-1}^{1} d\eta_1 \eta_1^{g+b} \right]$$

$$\times \left[\sum_{c,d} \delta^*_{\ell cd} \int_1^\infty d\xi_2 e^{-2\alpha\xi_2} \xi_2^{r+c} \int_{-1}^{1} d\eta_2 \eta_2^{s+d} \right] \tag{2.26}$$

Now

$$\int_{-1}^{1} d\eta\, \eta^n = \begin{cases} 0 \,;\, n \text{ odd} \\ \frac{2}{n+1} \,;\, n \text{ even} \end{cases}$$

and

$$\int_1^\infty dx\, e^{-2\alpha x} x^n dx = A_n(2\alpha) = \frac{e^{-2\alpha} n!}{(2\alpha)^{n+1}} \sum_{k=0}^{n} \frac{(2\alpha)^k}{k!} \tag{2.27}$$

The functions $A_n(x)$ are well known and will be developed in detail when we consider the reduction of eq. 2.10. Inspection of the expressions for Σ_k, eq. 2.8, show that if g is even then Σ_{kpg} is even in η for $k \leq 5$ and odd for $k=6,7$. The reverse is true for g odd. The odd functions in η dissappear upon integration, hence

$$\langle \Sigma_{kpg} | \Sigma^*_{\ell rs} \rangle = \frac{\pi^2 R^6}{4} Q_{kpg} Q^*_{\ell rs} \tag{2.28}$$

$$Q^{(*)}_{kpg} = \begin{cases} \sum_{a,b} \delta^{(*)}_{kab} (g+b+1)^{-1} A_{p+a}(2\alpha) \,;\, \begin{matrix} g \text{ even } \& \ k \leq 5 \\ g \text{ odd } \& \ k = 6,7 \end{matrix} \\ 0 \quad ;\, \text{otherwise} \end{cases}$$

To reduce eq. 2.10 we follow the procedure of Rüdenberg.[16] We will solve the problem in a somewhat general way using eq. 2.25 and the Von Neumann expansion, eq. 2.19. We integrate the angular parts immediately using eqs 2.20 and observe that the integrals factor out. Thus

$$\left[\varphi^{M}_{kpq} \middle| \varphi^{M*}_{jrs}\right]$$

$$= \frac{R^5}{32} \sum_{L=0}^{\infty} \sum_{a,b} \sum_{c,d} \delta_{kab}\, \delta^{*}_{jcd} \int_1^{\infty}\!\!\int_1^{\infty}\!\!\int_{-1}^{1}\!\!\int_{-1}^{1} d\xi_1\, d\xi_2\, d\eta_1\, d\eta_2 \int_0^{2\pi}\!\!\int_0^{2\pi} d\varphi_1\, d\varphi_2$$

$$\times\, e^{-2\alpha(\xi_1+\xi_2)}\, \xi_1^{p+a}\, \eta_1^{q+b}\, \xi_2^{r+c}\, \eta_2^{s+d} \cos m\varphi_1 \cos m\varphi_2$$

$$\times \left[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)\right]^{\frac{m}{2}}$$

$$\times \sum_{i=0}^{L} (-1)^i\, D_L^i\, P_L^i(\xi_<)\, Q_L^i(\xi_>)\, P_L^i(\eta_1)\, P_L^i(\eta_2) \cos i(\varphi_1-\varphi_2)$$

$$= \frac{R^5}{32} C(m) \sum_{L=0}^{\infty} \sum_{a,b} \sum_{c,d} \delta_{kab}\, \delta^{*}_{jcd}\, \mathbb{D}_L^m \int_{-1}^{1} P_L^m(\eta_1)\, \eta_1^{q+b} (1-\eta_1^2)^{\frac{m}{2}} d\eta_1$$

$$\times \int_{-1}^{1} P_L^m(\eta_2)\, \eta_2^{s+d} (1-\eta_2^2)^{\frac{m}{2}} d\eta_2$$

$$\times (-1)^m \int_1^{\infty} d\xi_1\, e^{-2\alpha\xi_1}\, \xi_1^{p+a} (\xi_1^2-1)^{\frac{m}{2}} \left[Q_L^m(\xi_1) \int_1^{\xi_1} d\xi_2\, P_L^m(\xi_2)\, e^{-2\alpha\xi_2} (\xi_2^2-1)^{\frac{m}{2}} \xi_2^{r+c} \right.$$

$$\left. + P_L^m(\xi_1) \int_{\xi_1}^{\infty} Q_L^m(\xi_2)\, e^{-2\alpha\xi_2} (\xi_2^2-1)^{\frac{m}{2}} \xi_2^{r+c}\, d\xi_2 \right] \qquad (2.29)$$

where

$$C(m) = \begin{cases} 2\pi^2 & ;\ m=0 \\ \pi^2 & ;\ m \geq 1 \end{cases}$$

$$\mathbb{D}_L^m = 2(2L+1)\left[\frac{(L-m)!}{(L+m)!}\right]^2 \text{ for all } m \geq 0$$

Let

$$\beta_j^{mL} = \int_{-1}^{1} P_L^m(x)(1-x^2)^{\frac{m}{2}} x^j \, dx \qquad (2.30)$$

Since[17]

$$\int_{-1}^{1} P_L^m(x)\, P_R^m(x)\, dx = \begin{cases} 0 \;; R \neq L \\ \dfrac{2}{(2L+1)} \dfrac{(L+m)!}{(L-m)!} \;; R = L \text{ and } L \geq M \end{cases} \qquad (2.31)$$

β_j^{mL} may be defined by the expansion

$$(1-x^2)^{\frac{m}{2}} x^j = \sum_{L=M}^{\infty} \beta_j^{mL} P_L^m(x) \frac{(2L+1)}{2} \frac{(L-m)!}{(L+m)!} \qquad (2.32)$$

as may be seen by multiplying eq. 2.32 by $P_R^M(x)$ and integrating using eq. 2.31 and comparing with eq. 2.30. But we may rewrite eq. 2.32 using the relation[21]

$$P_L^m(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m P_L(x)}{dx^m}$$

Then

$$x^j = \sum_{L=M}^{\infty} \beta_j^{mL} \frac{d^m P_L(x)}{dx^m} \frac{(2L+1)}{2} \frac{(L-m)!}{(L+M)!} \qquad (2.33)$$

But by setting $M=0$ in eq. 2.32 we get

$$x^j = \sum_{L=0}^{\infty} \beta_j^{0L} P_L(x) \frac{(2L+1)}{2} \qquad (2.34)$$

which we differentiate M times to find

$$\frac{j!}{(j-m)!} x^{j-M} = \sum_{L=0}^{\infty} \beta_j^{0L} \frac{d^m P_L(x)}{dx^m} \frac{(2L+1)}{2} \qquad (2.35)$$

We let $u=j-m$ in eq. 2.35 and note that $\frac{d^m P_L(x)}{dx^m}=0$ for $M>L$, hence

$$x^u = \sum_{L=M}^{\infty} \beta_{u+m}^{0L} \frac{d^m P_L(x)}{dx^m} \frac{(2L+1)}{2} \frac{u!}{(u+m)!} \qquad (2.36)$$

Comparison of eqs. 2.33 and 2.36 shows

$$\beta_j^{\,mL} = \frac{(L+m)!\; j!}{(L-m)!\,(j+m)!}\;\beta_{j+m}^{\,oL} \tag{2.37}$$

Now[18]

$$\beta_j^{\,oL} = \int_{-1}^{1} P_L(x)\, x^j\, dx$$

$$= \begin{cases} \dfrac{2^{L+1}\, j!\, \left(\frac{j+L}{2}\right)!}{\left(\frac{j-L}{2}\right)!\,(j+L+1)!} & ;\ j-L \geq 0 \text{ and even} \\ 0 ;\text{otherwise} \end{cases} \tag{2.38}$$

hence eq. 2.37 becomes

$$\beta_j^{\,mL} = \begin{cases} \dfrac{2^{L+1}(L+m)!\; j!\; \left(\frac{j+m+L}{2}\right)!}{(L-m)!\left(\frac{j+m-L}{2}\right)!\,(j+m+L+1)!} & ;\ j+m-L \geq 0 \text{ and even} \\ 0 ;\text{otherwise} \end{cases} \tag{2.39}$$

Turning now to the integrals over ξ_1, ξ_2 in eq. 2.29 we define

$$\mathcal{I}_{n\bar{n}}^{\,mL}(a) = \int_1^\infty e^{-a\xi}\xi^n(\xi^2-1)^{\frac{m}{2}} \Big[Q_L^m(\xi) \int_1^\xi P_L^m(x)\, e^{-ax}(x^2-1)^{\frac{m}{2}} x^{\bar{n}}\, dx$$

$$+ P_L^m(\xi) \int_\xi^\infty Q_L^m(x)\, e^{-ax}(x^2-1)^{\frac{m}{2}} x^{\bar{n}}\, dx \Big] d\xi \tag{2.40}$$

We observe that, integrating by parts,

$$\int_1^\infty d\xi\, e^{-a\xi}\xi^n(\xi^2-1)^{\frac{m}{2}} P_L^m(\xi) \int_\xi^\infty Q_L^m(x)\, e^{-\bar{a}x}(x^2-1)^{\frac{m}{2}} x^{\bar{n}}\, dx$$

$$= -Q_L^m(\xi)\, e^{-\bar{a}\xi}(\xi^2-1)^{\frac{m}{2}}\xi^{\bar{n}} \int_1^\xi e^{-ax} x^n (x^2-1)^{\frac{m}{2}} P_L^m(x)\, dx \,\Big|_{\xi=1}^{\infty}$$

$$+ \int_1^\infty Q_L^m(\xi)\, e^{-\bar{a}\xi}(\xi^2-1)^{\frac{m}{2}}\xi^{\bar{n}} \int_1^\xi P_L^m(x)\, e^{-ax} x^n (x^2-1)^{\frac{m}{2}}\, dx\, d\xi$$

$$= \int_1^\infty Q_L^m(\xi)\, e^{-\bar{a}\xi}(\xi^2-1)^{\frac{m}{2}}\xi^{\bar{n}} \int_1^\xi P_L^m(x)\, e^{-ax} x^n (x^2-1)^{\frac{m}{2}}\, dx\, d\xi \tag{2.41}$$

since the first term is zero at the limits as may be determined by the usual methods for indeterminant forms. From eq. 2.40 we find

$$\mathcal{I}_{n\bar{n}}^{mL}(a) = \int_1^\infty d\xi\, e^{-a\xi}\xi^n(\xi^2-1)^{\frac{m}{2}} Q_L^m(\xi)\int_1^\xi P_L^m(x)\, e^{-ax}(x^2-1)^{\frac{m}{2}} x^{\bar{n}} dx$$

$$+\int_1^\infty d\xi\, e^{-a\xi}\xi^{\bar{n}}(\xi^2-1)^{\frac{m}{2}} Q_L^m(\xi)\int_1^\xi dx\, e^{-ax} x^{\bar{n}}(x^2-1)^{\frac{m}{2}} P_L^m(x)$$

$$= \mathcal{I}_{\bar{n}n}^{mL}(a) \qquad (2.42)$$

It is useful to notice that

$$\frac{d}{d\xi}\left(\int_1^\xi dx\, P_L^m(x)\, e^{-\bar{a}x} x^{\bar{n}}(x^2-1)^{\frac{m}{2}}\int_1^\xi dx\, P_L^m(x)\, e^{-ax}x^n(x^2-1)^{\frac{m}{2}}\right)$$

$$= P_L^m(x)\, e^{-\bar{a}x} x^{\bar{n}}(x^2-1)^{\frac{m}{2}}\int_1^\xi dx\, P_L^m(x)\, e^{-ax} x^n(x^2-1)^{\frac{m}{2}}$$

$$+ P_L^m(x)\, e^{-ax}x^n(x^2-1)^{\frac{m}{2}}\int_1^\xi dx\, P_L^m(x)\, e^{-\bar{a}x} x^{\bar{n}}(x^2-1)^{\frac{m}{2}} \qquad (2.43)$$

Then we may write eq. 2.42 as

$$\mathcal{I}_{n\bar{n}}^{mL}(a) = \int_1^\infty d\xi\, \frac{Q_L^m(\xi)}{P_L^m(\xi)}\, \frac{d}{d\xi}\left(\int_1^\xi P_L^m(x)\, e^{-ax} x^{\bar{n}}(x^2-1)^{\frac{m}{2}}dx\int_1^\xi P_L^m(x)\, e^{-ax}x^n(x^2-1)^{\frac{m}{2}}dx\right) \qquad (2.44)$$

and integrate by parts in eq. 2.44 to obtain

$$\mathcal{I}_{n\bar{n}}^{mL}(a) = \frac{Q_L^m(\xi)}{P_L^m(\xi)}\int_1^\xi P_L^m(x)\, e^{-ax}x^{\bar{n}}(x^2-1)^{\frac{m}{2}}dx\int_1^\xi P_L^m(x)e^{-ax}x^n(x^2-1)^{\frac{m}{2}}dx\,\Bigg|_{\xi=1}^{\infty}$$

$$-\int_1^\infty d\xi\, \frac{d}{d\xi}\left(\frac{Q_L^m(\xi)}{P_L^m(\xi)}\right)\int_1^\xi P_L^m(x)\, e^{-ax}x^{\bar{n}}(x^2-1)^{\frac{m}{2}}dx\int_1^\xi P_L^m(x)e^{-ax}x^n(x^2-1)^{\frac{m}{2}}dx \qquad (2.45)$$

But the first term vanishes at the limits and[19]

$$\frac{d}{d\xi}\left(\frac{Q_L^m(\xi)}{P_L^m(\xi)}\right) = \frac{Q_L^{m\prime}(\xi)\,P_L^m(\xi) - P_L^{m\prime}(\xi)\,Q_L^m(\xi)}{\left[P_L^m(\xi)\right]^2}$$

$$= \frac{(-1)^{m+1}\,(L+m)!}{(\xi^2-1)\,(L-m)!\,\left[P_L^m(\xi)\right]^2} \qquad (2.46)$$

Use of eq. 2.46 in eq. 2.45 gives

$$\mathcal{I}_{n\bar{n}}^{mL}(a) = \frac{(-1)^m (L+m)!}{(L-m)!}\int_1^\infty (\xi^2-1)^{-1}\left[P_L^m(\xi)\right]^{-1}\int_1^\xi dx\, P_L^m(x)\, e^{-ax} x^{\bar{n}} (x^2-1)^{\frac{m}{2}}$$

$$\times \left[P_L^m(\xi)\right]^{-1}\int_1^\xi dx\, P_L^m(x)\, e^{-ax} x^{n} (x^2-1)^{\frac{m}{2}}\, d\xi$$

$$= \frac{(-1)^m (L+m)!}{(L-m)!}\int_1^\infty d\xi\, (\xi^2-1)^{-1}\, f_{\bar{n}}^{mL}(\xi,a)\, f_n^{mL}(\xi,a) \qquad (2.47)$$

where

$$f_n^{mL}(\xi,a) = \left[P_L^m(\xi)\right]^{-1}\int_1^\xi dx\, P_L^m(x)\, e^{-ax} x^n (x^2-1)^{\frac{m}{2}}$$

Then we may rewrite eq. 2.29 using eqs. 2.30, 2.39, 2.40, and 2.47

$$\left[\varphi_{kpq}^{M}\,\middle|\,\varphi_{\ell rs}^{M*}\right] = \frac{R^5}{32}\, C(M) \sum_{L=0}^{\infty}\sum_{a,b}\sum_{c,d} \delta_{kab}\, \delta_{\ell cd}^{*}\, \mathbb{D}_L^M\, \beta_{q+b}^{mL}\, \beta_{s+d}^{mL}$$

$$\times (-1)^M\, \mathcal{I}_{p+a,r+c}^{mL}(2\alpha) \qquad (2.48)$$

We now define

$$\Phi_{n\bar{n}}^{mL}(a) = \frac{(-1)^m (L-m)!}{(L+m)!}\, \mathcal{I}_{n\bar{n}}^{mL}(a) \qquad (2.49)$$

and

$$B_j^{mL} = \frac{1}{2}\left[\frac{(L+m)!}{(L-m)!}\, \mathbb{D}_L^m\right]^{\frac{1}{2}} \beta_j^{mL} \qquad (2.50)$$

Eq. 2.48 now becomes

$$\left[\varphi_{kpq}^{m} \middle| \varphi_{\ell rs}^{m*}\right] = \frac{R^5}{8} C(m) \sum_{L=0}^{\infty} \sum_{a,b,c,d}' \delta_{kab}\, \delta_{\ell cd}^{*}\, B_{q+b}^{mL}\, B_{s+d}^{mL}\, \Phi_{p+a,r+c}^{mL}(2\alpha) \quad (2.51)$$

where

$$B_j^{mL} = \begin{cases} \left[\dfrac{2(2L+1)(L+m)!}{(L-m)!}\right]^{\frac{1}{2}} \dfrac{2^L j!\left(\frac{j+m+L}{2}\right)!}{\left(\frac{j+m-L}{2}\right)!\,(j+m+L+1)!} & j+m-L \geq 0 \text{ and even} \\ 0\,; \text{ otherwise} \end{cases} \quad (2.52)$$

and (see eq. 2.47)

$$\Phi_{n,\bar{n}}^{mL}(\alpha) = \int_1^{\infty} d\xi\, (\xi^2-1)^{-1} f_n^{mL}(\xi,\alpha)\, f_{\bar{n}}^{mL}(\xi,\alpha) \quad (2.53)$$

Kolos and Roothaan evaluated the $\Phi_{n,\bar{n}}^{mL}(\alpha)$ by numerical integration for $m=0$ and then applied a recursion relation, to be derived later (see eq. 2.113), to obtain the integrals for $m=1, 2$. We will follow Rüdenberg and develop the $\Phi_{n,\bar{n}}^{mL}(\alpha)$ by recursion. In practice, however, recursion relations often lead to rapid loss of significant figures when small differences of large numbers are involved. Further discussion is best postponed until after the relations are developed.

We now proceed with the reduction of eq. 2.53 by considering the related integrals defined by

$$\varphi_{n,\bar{n}}^{mL}(\alpha,\bar{\alpha}) = \int_1^{\infty} d\xi\, (\xi^2-1)^{-1} f_n^{mL}(\xi,\alpha)\, f_{\bar{n}}^{mL}(\xi,\bar{\alpha}) \quad (2.54)$$

Then

$$\Phi_{n,\bar{n}}^{mL}(\alpha) = \varphi_{n,\bar{n}}^{mL}(\alpha,\alpha) \quad (2.55)$$

Inspection of the reduction of the integrals $\mathcal{I}_{n,\bar{n}}^{mL}(\alpha)$ (see eqs. 2.40-2.47) shows that we may also write

$$\varphi_{n,\bar{n}}^{mL}(\alpha,\bar{\alpha}) = \frac{(-1)^m (L-m)!}{(L+m)!} \int_1^\infty d\xi\, e^{-\alpha\xi} \xi^n (\xi^2-1)^{\frac{m}{2}}$$

$$\times \left[Q_L^m(\xi) \int_1^\xi dx\, P_L^m(x) e^{-\bar{\alpha}x} x^{\bar{n}} (x^2-1)^{\frac{m}{2}} + P_L^m(\xi) \int_1^\xi dx\, Q_L^m(x) e^{-\bar{\alpha}x} x^{\bar{n}} (x^2-1)^{\frac{m}{2}} \right]$$

$$= \frac{(-1)^m (L-m)!}{(L+m)!} \int_1^\infty d\xi \left[e^{-\alpha\xi} \xi^n (\xi^2-1)^{\frac{m}{2}} Q_L^m(\xi) \int_1^\xi dx\, P_L^m(x) e^{-\bar{\alpha}x} x^{\bar{n}} (x^2-1)^{\frac{m}{2}} \right.$$

$$\left. + e^{-\bar{\alpha}\xi} \xi^{\bar{n}} (\xi^2-1)^{\frac{m}{2}} Q_L^m(\xi) \int_1^\xi dx\, P_L^m(x) e^{-\alpha x} x^n (x^2-1)^{\frac{m}{2}} \right] \qquad (2.56)$$

Consider first the functions for $M=L=0$. We have (from eq. 2.54)

$$\varphi_{n,\bar{n}}^{00}(\alpha,\bar{\alpha}) = \int_1^\infty d\xi\, (\xi^2-1)^{-1} \int_1^\xi dx\, e^{-\alpha x} x^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}}$$

$$= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \int_1^\infty d\xi\, (\xi^2-1)^{-1} \int_1^\xi dx\, e^{-\alpha x} \int_1^\xi dx\, e^{-\bar{\alpha}x}$$

$$= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \varphi_{0,0}^{00}(\alpha,\bar{\alpha}) \qquad (2.57)$$

Since, from 2.54,

$$\varphi_{00}^{00}(\alpha,\bar{\alpha}) = \int_1^\infty d\xi\, (\xi^2-1)^{-1} \int_1^\xi dx\, e^{-\alpha x} \int_1^\xi dx\, e^{-\bar{\alpha}x} \qquad (2.58)$$

and

$$\int_1^\xi e^{-ax} dx = - \frac{e^{-ax}}{a} \bigg|_{x=1}^{\xi} = \frac{e^{-a} - e^{-a\xi}}{a}$$

we find

$$\varphi_{00}^{00}(\alpha,\bar{\alpha}) = \frac{1}{\alpha\bar{\alpha}} \int_1^\infty d\xi\, (\xi^2-1)^{-1} (e^{-\alpha} - e^{-\alpha\xi})(e^{-\bar{\alpha}} - e^{-\bar{\alpha}\xi})$$

$$= \frac{1}{\alpha\bar{\alpha}} \int_1^\infty d\xi\, (\xi^2-1)^{-1} \left(e^{-(\alpha+\bar{\alpha})} - e^{-\alpha} e^{-\bar{\alpha}\xi} - e^{-\bar{\alpha}} e^{-\alpha\xi} + e^{-(\alpha+\bar{\alpha})\xi} \right) \qquad (2.59)$$

We use the integrals

$$\int_1^\infty \frac{d\xi}{(\xi^2-1)} = \frac{1}{2}\int_1^\infty \frac{d\xi}{\xi-1} - \frac{1}{2}\int_1^\infty \frac{d\xi}{\xi+1} = \lim_{x\to 0} \frac{1}{2}(\ln 2 - \ln x) \qquad (2.60)$$

and

$$\int_1^\infty \frac{e^{-a\xi}}{\xi^2-1}d\xi = \frac{1}{2}\int_1^\infty \frac{e^{-a\xi}}{\xi-1}d\xi - \frac{1}{2}\int_1^\infty \frac{e^{-a\xi}}{\xi+1}d\xi$$

$$= \lim_{x\to 0} \frac{e^{-a}}{2}\int_x^\infty \frac{e^{-a\xi}}{\xi}d\xi - \frac{e^{a}}{2}\int_2^\infty \frac{e^{-a\xi}}{\xi}d\xi$$

$$= \lim_{x\to 0} \frac{e^{-a}}{2}\int_{-ax}^{-\infty} \frac{e^{\xi}}{\xi}d\xi - \frac{e^{a}}{2}\int_{-2a}^{-\infty} \frac{e^{\xi}}{\xi}d\xi$$

$$= \lim_{x\to 0} -\frac{e^{-a}}{2}\,Ei(-ax) + \frac{e^{a}}{2}\,Ei(-2a) \qquad (2.61)$$

where [20]

$$Ei(x) = \int_{-\infty}^{x} \frac{e^{t}}{t}dt = \int_{-\infty}^{1} \frac{e^{xt}}{t}dt = C + \ln|x| + \sum_{n=1}^{\infty} \frac{x^n}{n\cdot n!} \quad ; x<0 \qquad (2.62)$$

C = Euler's constant = .577215....

We then rewrite eq. 2.59 as

$$\varphi_{oo}^{oo}(\alpha,\bar\alpha) = \frac{e^{-(\alpha+\bar\alpha)}}{\alpha\bar\alpha}\left[\int_1^\infty d\xi(\xi^2-1)^{-1} - e^{-\bar\alpha}\int_1^\infty \frac{e^{-\bar\alpha\xi}}{(\xi^2-1)}d\xi \right.$$

$$\left. - e^{-\alpha}\int_1^\infty \frac{e^{-\alpha\xi}}{(\xi^2-1)}d\xi + e^{\alpha+\bar\alpha}\int_1^\infty \frac{e^{-(\alpha+\bar\alpha)\xi}}{(\xi^2-1)}d\xi\right] \qquad (2.63)$$

and insert eqs. 2.60 and 2.61 to find

$$\varphi_{oo}^{oo}(\alpha,\bar\alpha) = \frac{e^{-(\alpha+\bar\alpha)}}{\alpha\bar\alpha}\left[\frac{1}{2}\ln 2 - \frac{1}{2}\ln x + \frac{1}{2}Ei(-\bar\alpha x) - \frac{e^{2\bar\alpha}}{2}Ei(-2\bar\alpha) + \frac{1}{2}Ei(-\alpha x)\right.$$

$\lim x\to 0$

$$\left. - \frac{e^{2\alpha}}{2}Ei(-2\alpha) - \frac{1}{2}Ei(-[\alpha+\bar\alpha]x) + \frac{e^{2(\alpha+\bar\alpha)}}{2}Ei(-2[\alpha+\bar\alpha])\right] \qquad (2.64)$$

Then employing eq. 2.62 we find the infinities cancel and we have

$$\varphi_{00}^{00}(\alpha,\bar{\alpha}) = \frac{e^{-(\alpha+\bar{\alpha})}}{2\alpha\bar{\alpha}}\Big[C + \ln 2 + \ln\alpha + \ln\bar{\alpha} - \ln(\alpha+\bar{\alpha}) - e^{2\bar{\alpha}}Ei(-2\bar{\alpha})$$

$$- e^{2\alpha}Ei(-2\alpha) + e^{2(\bar{\alpha}+\alpha)}Ei(-2[\alpha+\bar{\alpha}])\Big]$$

$$= \frac{e^{-(\alpha+\bar{\alpha})}}{\alpha\bar{\alpha}}\Big[\mathcal{E}(\alpha) + \mathcal{E}(\bar{\alpha}) - \mathcal{E}(\alpha+\bar{\alpha})\Big] \tag{2.65}$$

where

$$\mathcal{E}(x) = \frac{1}{2}\Big[C + \ln 2x - e^{2x}Ei(-2x)\Big]$$

Now define the functions $G_n(x)$ by the relations

$$G_n(x) = (-1)^n \frac{d^n}{dx^n}G_o(x) \quad ; n \geq 0 \tag{2.66}$$

$$G_o(x) = e^{-x}\mathcal{E}(x)$$

and the familiar $A_n(x)$ (see eq. 2.27)

$$A_n(x) = \int_1^\infty dt\, e^{-xt}t^n = (-1)^n \frac{d^n}{dx^n}A_o(x) \quad ; n \geq 0 \tag{2.67}$$

$$A_o(x) = \frac{e^{-x}}{x}$$

We may now write eq. 2.65 as

$$\varphi_{00}^{00}(\alpha,\bar{\alpha}) = \frac{1}{\alpha\bar{\alpha}}\Big[e^{-\bar{\alpha}}G_o(\alpha) + e^{-\alpha}G_o(\bar{\alpha}) - G_o(\alpha+\bar{\alpha})\Big] \tag{2.68}$$

We now examine the identity (from eq. 2.68)

$$(-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\Big[\alpha\bar{\alpha}\,\varphi_{00}^{00}(\alpha,\bar{\alpha})\Big] = (-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\Big[e^{-\bar{\alpha}}G_o(\alpha) + e^{-\alpha}G_o(\bar{\alpha}) - G_o(\alpha+\bar{\alpha})\Big]$$

$$= e^{-\bar{\alpha}} G_n(\alpha) + e^{-\alpha} G_n(\bar{\alpha}) - G_{n+\bar{n}}(\alpha+\bar{\alpha}) \qquad (2.69)$$

by virtue of the definition of $G_n(x)$. Using the handy formula for multiple differentiation of a product

$$\frac{d^n}{dx^n}\left[f(x)g(x)\right] = \sum_{i=0}^{n} \binom{n}{i} \frac{d^i f(x)}{dx^i} \frac{d^{n-i} g(x)}{dx^{n-i}} \quad ; \quad \binom{n}{i} = \frac{n!}{(n-i)!\, i!} \qquad (2.70)$$

we have

$$(-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \left[\alpha\bar{\alpha}\, \varphi_{00}^{00}(\alpha,\bar{\alpha})\right] = (-1)^{n+\bar{n}} \sum_{i=0}^{n} \sum_{j=0}^{\bar{n}} \binom{n}{i}\binom{\bar{n}}{j} \frac{\partial^{i+j}(\alpha\bar{\alpha})}{\partial\alpha^i \partial\bar{\alpha}^j}$$

$$\times \frac{\partial^{n+\bar{n}-i-j}}{\partial\alpha^{n-i}\partial\bar{\alpha}^{\bar{n}-j}} \varphi_{00}^{00}(\alpha,\bar{\alpha}) \qquad (2.71)$$

But (from eq. 2.57)

$$\frac{\partial^{n+\bar{n}-i-j}}{\partial\alpha^{n-i}\partial\bar{\alpha}^{\bar{n}-j}} \varphi_{00}^{00}(\alpha,\bar{\alpha}) = (-1)^{n+\bar{n}-i-j} \varphi_{n-i,\bar{n}-j}^{00}(\alpha,\bar{\alpha})$$

and

$$\frac{\partial^{i+j}(\alpha\bar{\alpha})}{\partial\alpha^i \partial\bar{\alpha}^j} = \begin{cases} \alpha\bar{\alpha} & ; \ i=j=0 \\ \alpha & ; \ i=0, j=1 \\ \bar{\alpha} & ; \ i=1, j=0 \\ 1 & ; \ i=j=1 \\ 0 & \text{otherwise} \end{cases}$$

Hence

$$(-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \left[\alpha\bar{\alpha}\, \varphi_{00}^{00}(\alpha,\bar{\alpha})\right] = (-1)^{n+\bar{n}}\Big[(-1)^{n+\bar{n}-2} n\bar{n}\, \varphi_{n-1,\bar{n}-1}^{00}(\alpha,\bar{\alpha}) + (-1)^{n+\bar{n}} \alpha\bar{\alpha}\, \varphi_{n,\bar{n}}^{00}(\alpha,\bar{\alpha})$$

$$+ (-1)^{n+\bar{n}-1} n\bar{\alpha}\, \varphi_{n-1,\bar{n}}^{00}(\alpha,\bar{\alpha}) + (-1)^{n+\bar{n}-1} \bar{n}\alpha\, \varphi_{n,\bar{n}-1}^{00}(\alpha,\bar{\alpha})\Big]$$

$$= n\bar{n}\, \varphi_{n-1,\bar{n}-1}^{00}(\alpha,\bar{\alpha}) + \alpha\bar{\alpha}\, \varphi_{n,\bar{n}}^{00}(\alpha,\bar{\alpha})$$

$$- n\bar{\alpha}\, \varphi_{n-1,\bar{n}}^{00}(\alpha,\bar{\alpha}) - \bar{n}\alpha\, \varphi_{n,\bar{n}-1}^{00}(\alpha,\bar{\alpha}) \qquad (2.72)$$

Using eq. 2.72, we rearrange eq. 2.69 to obtain the recursion formula

$$\varphi_{n,\bar{n}}^{oo}(\alpha,\bar{\alpha}) = \frac{1}{\alpha\bar{\alpha}}\Big[n\bar{\alpha}\,\varphi_{n-1,\bar{n}}^{oo}(\alpha,\bar{\alpha}) + \bar{n}\alpha\,\varphi_{n,\bar{n}-1}^{oo}(\alpha,\bar{\alpha}) - n\bar{n}\,\varphi_{n-1,\bar{n}-1}^{oo}(\alpha,\bar{\alpha})$$

$$+ e^{-\bar{\alpha}}G_n(\alpha) + e^{-\alpha}G_n(\bar{\alpha}) - G_n(\alpha+\bar{\alpha})\Big] \qquad (2.73)$$

Returning to the $G_n(x)$, eqs. 2.66, we have

$$G_1(x) = -\frac{d}{dx}G_o(x) = -\frac{d}{dx}\left(e^{-x}\mathcal{E}(x)\right)$$

$$= e^{-x}\mathcal{E}(x) - e^{-x}\frac{d\,\mathcal{E}(x)}{dx}$$

$$= e^{-x}\mathcal{E}(x) - \frac{e^{-x}}{2}\left\{\frac{1}{x} - 2e^{2x}Ei(-2x) + e^{2x}\frac{d}{dx}Ei(-2x)\right\} \qquad (2.74)$$

and (see eq. 2.62)

$$\frac{d}{dx}Ei(-2x) = \frac{d}{dx}\int_{-\infty}^{-2x}\frac{e^t}{t}dt = \frac{e^{-2x}}{x}$$

hence

$$G_1(x) = \frac{e^{-x}}{2}\left\{C + \ln 2x + e^{2x}Ei(-2x)\right\} \qquad (2.75)$$

and

$$G_2(x) = -\frac{d}{dx}G_1(x) = \frac{e^{-x}}{2}\left\{C + \ln 2x + e^{2x}Ei(-2x) - \frac{2}{x} - 2e^{2x}Ei(-2x)\right\}$$

$$= e^{-x}\mathcal{E}(x) - \frac{e^{-x}}{x}$$

$$= G_o(x) - A_o(x) \qquad (2.76)$$

Then for $n \geq 2$ use of eqs. 2.66 and 2.67 on eq. 2.76 yields the recursion formula for the $G_n(x)$.

$$G_n(x) = (-1)^n \frac{d^n}{dx^n} G_0(x) = (-1)^{n-2} \frac{d^{n-2}}{dx^{n-2}} G_2(x)$$

$$= (-1)^{n-2} \frac{d^{n-2}}{dx^{n-2}} G_0(x) - (-1)^{n-2} \frac{d^{n-2}}{dx^{n-2}} A_0(x)$$

$$= G_{n-2}(x) - A_{n-2}(x) \tag{2.77}$$

For the $A_n(x)$ we return to the definition, eq. 2.67, and integrate by parts

$$A_n(x) = \int_1^\infty e^{-xt} t^n dt$$

$$= -\frac{t^n e^{-xt}}{x}\Big|_{t=1}^{\infty} + \frac{n}{x}\int_1^\infty t^{n-1} e^{-xt} dt$$

$$= \frac{e^{-x}}{x} + \frac{n}{x} A_{n-1}(x)$$

$$= \frac{1}{x}\left[e^{-x} + n A_{n-1}(x)\right]$$

$$= A_0(x) + \frac{n}{x} A_{n-1}(x) \tag{2.78}$$

For the functions $\varphi_{n,\bar{n}}^{0L}(\alpha,\bar{\alpha})$ we may write (from eq. 2.56)

$$\varphi_{n\bar{n}}^{0L}(\alpha,\bar{\alpha}) = \int_1^\infty d\xi\, \varphi_L(\xi) \left\{ e^{-\alpha\xi} \xi^n \int_1^\xi dx\, P_L(x)\, e^{-\bar{\alpha}x} x^{\bar{n}} + e^{-\bar{\alpha}\xi} \xi^{\bar{n}} \int_1^\xi dx\, P_L(x)\, e^{-\alpha x} x^n \right\}$$

$$= \int_1^\infty d\xi \left\{ e^{-\alpha\xi} \xi^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}} R_L(x,\xi) + e^{-\bar{\alpha}\xi} \xi^{\bar{n}} \int_1^\xi dx\, e^{-\alpha x} x^n R_L(x,\xi) \right\} \tag{2.79}$$

where

$$R_L(x,\xi) = Q_L(\xi)\,P_L(x) \quad ; \quad L \geq 0 \tag{2.80}$$

We define the following functions:

$$S_L(x,\xi) = L\left[\xi\,Q_L(\xi)\,P_{L-1}(x) + x\,Q_{L-1}(\xi)\,P_L(x)\right] \quad ; \quad L \geq 1 \tag{2.81}$$

$$\psi_{n,\bar{n}}^{\,0L}(\alpha,\bar{\alpha}) = \int_1^{\infty} d\xi \left\{ e^{-\alpha\xi}\xi^n \int_1^{\xi} dx\, e^{-\bar{\alpha}x} x^{\bar{n}}\, S_L(x,\xi) + e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^{\xi} dx\, e^{-\alpha x} x^n\, S_L(x,\xi) \right\} \tag{2.82}$$

Using the following recursion relations for the Legendre functions[21]

$$L\,P_L(x) = (2L-1)\,x\,P_{L-1}(x) - (L-1)\,P_{L-2}(x) \quad ; \quad L \geq 2$$

$$L\,Q_L(\xi) = (2L-1)\,\xi\,Q_{L-1}(\xi) - (L-1)\,Q_{L-2}(\xi) \tag{2.83}$$

we find $(L \geq 2)$

$$L^2 Q_L(\xi)P_L(x) = (2L-1)^2\,\xi x\,Q_{L-1}(\xi)P_{L-1}(x) + (L-1)^2\,Q_{L-2}(\xi)P_{L-2}(x)$$
$$-(L-1)(2L-1)\left[\xi\,Q_{L-1}(\xi)P_{L-2}(x) + x\,Q_{L-2}(\xi)P_{L-1}(x)\right]$$

or

$$R_L(x,\xi) = \frac{1}{L^2}\left[(2L-1)^2\,\xi x\,R_{L-1}(x,\xi) + (L-1)^2 R_{L-2}(x,\xi) - \frac{(2L-1)(L-1)}{L} S_{L-1}(x,\xi)\right] \tag{2.84}$$

Then, using eq. 2.84, eq. 2.79 becomes (for $L \geq 2$)

$$\varphi_{n\bar{n}}^{\,0L}(\alpha,\bar{\alpha}) = \frac{1}{L^2}\left[(2L-1)^2\,\varphi_{n+1,\bar{n}+1}^{\,0,L-1}(\alpha,\bar{\alpha}) + (L-1)^2\,\varphi_{n,\bar{n}}^{\,0,L-2}(\alpha,\bar{\alpha}) - \frac{(2L-1)(L-1)}{L}\,\psi_{n,\bar{n}}^{\,0,L-1}(\alpha,\bar{\alpha})\right] \tag{2.85}$$

Applying the relations 2.83 to eq. 2.81 we find a relation for $S_L(x,\xi)$ for $L \geq 3$.

$$S_L(x,\xi) = L\left[\frac{\xi P_{L-1}(x)}{L}\left([2L-1]\xi Q_{L-1}(\xi) - [L-1]\, Q_{L-2}(\xi)\right)\right.$$

$$\left. + \frac{x Q_{L-1}(\xi)}{L}\left([2L-1]x P_{L-1}(x) - [L-1]\, P_{L-2}(x)\right)\right]$$

$$= (2L-1)(\xi^2+x^2)\, Q_{L-1}(\xi)\, P_{L-1}(x)$$

$$-(L-1)\left[\xi\, Q_{L-2}(\xi)\, P_{L-1}(x) + x\, Q_{L-1}(\xi)\, P_{L-2}(x)\right] \qquad (2.86)$$

and $(L \geq 3)$

$$\mathcal{S} = \xi\, Q_{L-2}(\xi)\, P_{L-1}(x) + x\, Q_{L-1}(\xi)\, P_{L-2}(x)$$

$$= \frac{\xi Q_{L-2}(\xi)}{(L-1)}\left[(2L-3)\, x\, P_{L-2}(x) - (L-2)\, P_{L-3}(x)\right]$$

$$+ \frac{x P_{L-2}(x)}{(L-1)}\left[(2L-3)\,\xi\, Q_{L-2}(\xi) - (L-2)\, Q_{L-3}(\xi)\right]$$

$$= \frac{2(2L-3)}{(L-1)}\, x\xi\, Q_{L-2}(\xi)\, P_{L-2}(x) - \frac{(L-2)}{(L-1)}\left[\xi\, Q_{L-2}(\xi)\, P_{L-3}(x) + x\, Q_{L-3}(\xi)\, P_{L-2}(x)\right]$$

which gives the relation $(L \geq 3)$

$$S_L(x,\xi) = (2L-1)(x^2+\xi^2)\, R_{L-1}(x,\xi) - 2(2L-3)\, x\xi\, R_{L-2}(x,\xi) - S_{L-2}(x,\xi) \qquad (2.87)$$

or, upon substitution into eq. 2.82

$$\psi_{n,\bar{n}}^{\,0L}(\alpha,\bar{\alpha}) = (2L-1)\left[\varphi_{n+2,\bar{n}}^{\,0,L-1}(\alpha,\bar{\alpha}) + \varphi_{n,\bar{n}+2}^{\,0,L-1}(\alpha,\bar{\alpha})\right] - 2(2L-3)\,\varphi_{n+1,\bar{n}+1}^{\,0,L-2}(\alpha,\bar{\alpha}) - \psi_{n,\bar{n}}^{\,0,L-2}(\alpha,\bar{\alpha}) \qquad (2.88)$$

Here we have observed that

$$\int_1^\infty d\xi\left(e^{-\alpha\xi}\xi^n\int_1^\xi dx\, e^{-\bar\alpha x}x^{\bar n}(x^2+\xi^2)R_{L-1}(x,\xi)+e^{-\bar\alpha\xi}\xi^{\bar n}\int_1^\xi dx\, e^{-\alpha x}x^n(x^2+\xi^2)R_{L-1}(x,\xi)\right)$$

$$=\int_1^\infty d\xi\left(e^{-\alpha\xi}\xi^n\int_1^\xi dx\, e^{-\bar\alpha x}x^{\bar n+2}R_{L-1}(x,\xi)+e^{-\alpha\xi}\xi^{n+2}\int_1^\xi dx\, e^{-\bar\alpha x}x^{\bar n}R_{L-1}(x,\xi)\right)$$

$$+\int_1^\infty d\xi\left(e^{-\bar\alpha\xi}\xi^{\bar n}\int_1^\xi dx\, e^{-\alpha x}x^{n+2}R_{L-1}(x,\xi)+e^{-\bar\alpha\xi}\xi^{\bar n+2}\int_1^\xi dx\, e^{-\alpha x}x^{n}R_{L-1}(x,\xi)\right)$$

$$=\int_1^\infty d\xi\left(e^{-\alpha\xi}\xi^{n+2}\int_1^\xi dx\, e^{-\bar\alpha x}x^{\bar n}R_{L-1}(x,\xi)+e^{-\bar\alpha\xi}\xi^{\bar n}\int_1^\xi dx\, e^{-\alpha x}x^{\bar n+2}R_{L-1}(x,\xi)\right)$$

$$+\int_1^\infty d\xi\left(e^{-\alpha\xi}\xi^{n}\int_1^\xi dx\, e^{-\bar\alpha x}x^{\bar n+2}R_{L-1}(x,\xi)+e^{-\bar\alpha\xi}\xi^{\bar n+2}\int_1^\xi dx\, e^{-\alpha x}x^{n}R_{L-1}(x,\xi)\right)$$

$$=\varphi^{0,L-1}_{n+2,\bar n}(\alpha,\bar\alpha)+\varphi^{0,L-1}_{n,\bar n+2}(\alpha,\bar\alpha)$$

To extend the relations to small L we note that (see eqs. 2.80-3)

$$R_1(x,\xi)=Q_1(\xi)P_1(x)=x\left\{\xi Q_0(\xi)-1\right\}$$

$$=x\xi R_0(x,\xi)-x \tag{2.84*}$$

and

$$S_2(x,\xi)=2\left\{xQ_1(\xi)P_2(x)+\xi Q_2(\xi)P_1(x)\right\}$$

$$=xQ_1(\xi)\Big[3xP_1(x)-P_0(x)\Big]+\xi P_1(x)\Big[3\xi Q_1(\xi)-Q_0(\xi)\Big]$$

$$=3(x^2+\xi^2)Q_1(\xi)P_1(x)-Q_1(\xi)P_1(x)-\xi x\, Q_0(\xi)P_0(x)$$

$$=3(x^2+\xi^2)R_1(x,\xi)-R_1(x,\xi)-x\xi R_0(x,\xi)$$

$$=3(x^2+\xi^2)R_1(x,\xi)-x$$

$$S_1(x,\xi) = xQ_0(\xi)P_1(x) + \xi\, Q_1(\xi)P_0(x)$$

$$= x^2 Q_0(\xi)P_0(x) + \xi P_0(x)\left[\xi Q_0(\xi) - 1\right]$$

$$= (x^2+\xi^2)R_0(x,\xi) - (\xi + x) + x \qquad (2.87*)$$

We now define the functions

$$J_{n\bar{n}}(\alpha,\bar{\alpha}) = \int_1^\infty d\xi \left(e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^\xi dx\, e^{-\alpha x} x^n (\xi + x) + e^{-\alpha\xi}\xi^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}} (\xi + x) \right) \qquad (2.89)$$

$$F_{n\bar{n}}(\alpha,\bar{\alpha}) = \int_1^\infty d\xi \left(e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^\xi dx\, e^{-\alpha x} x^{n+1} + e^{-\alpha\xi}\xi^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}+1} \right) \qquad (2.90)$$

Hence from eqs. 2.79 and 2.82 we have

$$\varphi^{01}_{n\bar{n}}(\alpha,\bar{\alpha}) = \varphi^{00}_{n+1,\bar{n}+1}(\alpha,\bar{\alpha}) - F_{n\bar{n}}(\alpha,\bar{\alpha}) \qquad (2.85*)$$

$$\psi^{01}_{n\bar{n}}(\alpha,\bar{\alpha}) = \varphi^{00}_{n+2,\bar{n}}(\alpha,\bar{\alpha}) + \varphi^{00}_{n,\bar{n}+2}(\alpha,\bar{\alpha}) - J_{n\bar{n}}(\alpha,\bar{\alpha}) + F_{n\bar{n}}(\alpha,\bar{\alpha})$$

$$\psi^{02}_{n\bar{n}}(\alpha,\bar{\alpha}) = 3\left[\varphi^{01}_{n+2,\bar{n}}(\alpha,\bar{\alpha}) + \varphi^{01}_{n,\bar{n}+2}(\alpha,\bar{\alpha})\right] - F_{n\bar{n}}(\alpha,\bar{\alpha}) \qquad (2.88*)$$

Eq. 2.89 may be written

$$J_{n\bar{n}}(\alpha,\bar{\alpha}) = \int_1^\infty d\xi \left[e^{-\alpha\xi}\xi^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}} (x+\xi) + e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^\xi dx\, e^{-\alpha x} x^n (x+\xi) \right]$$

$$= \int_1^\infty d\xi \Big(e^{-\alpha\xi}\xi^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}+1} + e^{-\alpha\xi}\xi^{n+1} \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}}$$

$$+ e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^\xi dx\, e^{-\alpha x} x^{n+1} + e^{-\bar{\alpha}\xi}\xi^{\bar{n}+1} \int_1^\xi dx\, e^{-\alpha x} x^n \Big)$$

$$= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \int_1^\infty d\xi \Big[e^{-\alpha\xi} \int_1^\xi dx\, e^{-\bar{\alpha}x} x + e^{-\alpha\xi}\xi \int_1^\xi dx\, e^{-\bar{\alpha}x}$$

$$+ e^{-\bar{\alpha}\xi} \int_1^\xi dx\, e^{-\alpha x} x + e^{-\bar{\alpha}\xi}\xi \int_1^\xi dx\, e^{-\alpha x} \Big] \qquad (2.91)$$

We now note that the quantity in brackets in eq. 2.91 is just

$$[\;] = \frac{d}{d\xi}\left(\int_1^{\xi} dx\, e^{-\bar{\alpha}x}\int_1^{\xi} dx\, e^{-\alpha x}\, x + \int_1^{\xi} dx\, e^{-\alpha x}\int_1^{\xi} dx\, e^{-\bar{\alpha}x}\, x\right)$$

The first integration becomes trivial in eq. 2.91 and we have

$$J_{n\bar{n}}(\alpha,\bar{\alpha}) = (-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\left(\int_1^{\infty} dx\, e^{-\bar{\alpha}x}\int_1^{\infty} dx\, e^{-\alpha x}\, x + \int_1^{\infty} dx\, e^{-\alpha x}\int_1^{\infty} dx\, e^{-\bar{\alpha}x}\, x\right) \tag{2.92}$$

The remaining integrals are just the $A_n(\alpha)$ given by eq. 2.67:

$$J_{n\bar{n}}(\alpha,\bar{\alpha}) = (-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\Big(A_1(\alpha)A_0(\bar{\alpha}) + A_0(\alpha)A_1(\bar{\alpha})\Big)$$

$$= A_{n+1}(\alpha)A_n(\bar{\alpha}) + A_n(\alpha)A_{n+1}(\bar{\alpha}) \tag{2.93}$$

Turning to the $F_{n\bar{n}}(\alpha,\bar{\alpha})$, we have

$$F_{n\bar{n}}(\alpha,\bar{\alpha}) = \int_1^{\infty} d\xi\left(e^{-\alpha\xi}\xi^{n}\int_1^{\xi} dx\, e^{-\bar{\alpha}x}x^{\bar{n}+1} + e^{-\bar{\alpha}\xi}\xi^{\bar{n}}\int_1^{\xi} dx\, e^{-\alpha x}x^{n+1}\right)$$

$$= \frac{(-1)^{n+\bar{n}}\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\left[\int_1^{\infty} d\xi\left(e^{-\alpha\xi}\int_1^{\xi} dx\, e^{-\bar{\alpha}x}x + e^{-\bar{\alpha}\xi}\int_1^{\xi} dx\, e^{-\alpha x}x\right)\right] \tag{2.94}$$

Performing the integrations gives

$$F_{n\bar{n}}(\alpha,\bar{\alpha}) = (-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\int_1^{\infty} d\xi\left[e^{-\alpha\xi}\left(-\frac{e^{-\bar{\alpha}x}(\bar{\alpha}x+1)}{\bar{\alpha}^2}\Big|_{x=1}^{\xi}\right)\right.$$

$$\left. + e^{-\bar{\alpha}\xi}\left(-\frac{e^{-\alpha x}(\alpha x+1)}{\alpha^2}\Big|_{x=1}^{\xi}\right)\right]$$

$$= (-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\int_1^{\infty} d\xi\left[-\frac{(\alpha+\bar{\alpha})\xi e^{-(\alpha+\bar{\alpha})\xi}}{\alpha\bar{\alpha}} - \frac{(\alpha^2+\bar{\alpha}^2)}{\alpha^2\bar{\alpha}^2}e^{-(\alpha+\bar{\alpha})\xi}\right.$$

$$\left. + \frac{e^{-\bar{\alpha}}(\bar{\alpha}+1)e^{-\alpha\xi}}{\bar{\alpha}^2} + \frac{e^{-\alpha}(\alpha+1)e^{-\bar{\alpha}\xi}}{\alpha^2}\right]$$

$$= (-1)^{n+\bar{n}}\frac{\partial^{n+\bar{n}}}{\partial\alpha^n\partial\bar{\alpha}^{\bar{n}}}\left[\frac{-(\alpha+\bar{\alpha}+1)e^{-(\alpha+\bar{\alpha})}}{\alpha\bar{\alpha}(\alpha+\bar{\alpha})} - \frac{(\alpha^2+\bar{\alpha}^2)e^{-(\alpha+\bar{\alpha})}}{\alpha^2\bar{\alpha}^2(\alpha+\bar{\alpha})}\right.$$

$$+ \frac{(\bar{\alpha}+1)\, e^{-(\alpha+\bar{\alpha})}}{\alpha\bar{\alpha}^2} + \frac{(\alpha+1)\, e^{-(\alpha+\bar{\alpha})}}{\alpha^2\bar{\alpha}} \Bigg]$$

$$= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \left[\frac{e^{-(\alpha+\bar{\alpha})}\, \alpha\bar{\alpha}(1+\alpha+\bar{\alpha})}{\alpha^2\bar{\alpha}^2(\alpha+\bar{\alpha})} \right]$$

$$= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \left[\frac{e^{-\alpha}}{\alpha} \frac{e^{-\bar{\alpha}}}{\bar{\alpha}} + \frac{e^{-(\alpha+\bar{\alpha})}}{\alpha\bar{\alpha}(\alpha+\bar{\alpha})} \right]$$

$$= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \left[A_0(\alpha) A_0(\bar{\alpha}) + \frac{A_0(\alpha) A_0(\bar{\alpha})}{(\alpha+\bar{\alpha})} \right]$$

$$= A_n(\alpha) A_{\bar{n}}(\bar{\alpha}) + A_{n\bar{n}}(\alpha,\bar{\alpha}) \tag{2.95}$$

where we define

$$\left. \begin{aligned} A_{n,\bar{n}}(\alpha,\bar{\alpha}) &= (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} A_{00}(\alpha,\bar{\alpha}) \\ A_{00}(\alpha,\bar{\alpha}) &= \frac{1}{(\alpha+\bar{\alpha})} A_0(\alpha) A_0(\bar{\alpha}) \end{aligned} \right| \tag{2.96}$$

We examine the identity from eq. 2.96 (using eq. 2.67)

$$(-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} \left[(\alpha+\bar{\alpha}) A_{00}(\alpha,\bar{\alpha}) \right] = (-1)^{n+\bar{n}} \frac{\partial^{n+\bar{n}}}{\partial\alpha^n \partial\bar{\alpha}^{\bar{n}}} A_0(\alpha) A_0(\bar{\alpha})$$

$$= A_n(\alpha) A_{\bar{n}}(\bar{\alpha}) \tag{2.97}$$

Expanding the left-hand side using eq. 2.70 gives

$$A_n(\alpha) A_{\bar{n}}(\bar{\alpha}) = (-1)^{n+\bar{n}} \sum_{i=0}^{n} \sum_{j=0}^{\bar{n}} \binom{n}{i} \binom{\bar{n}}{j} \frac{\partial^{i+j} (\alpha+\bar{\alpha})}{\partial\alpha^i\, \partial\alpha^j} \frac{\partial^{n-i+\bar{n}-j}}{\partial\alpha^{n-i} \partial\bar{\alpha}^{\bar{n}-j}} A_{00}(\alpha,\bar{\alpha})$$

$$= (\alpha+\bar{\alpha}) A_{n\bar{n}}(\alpha,\bar{\alpha}) - n A_{n-1,\bar{n}}(\alpha,\bar{\alpha}) - \bar{n} A_{n,\bar{n}-1}(\alpha,\bar{\alpha})$$

or

$$A_{n,\bar{n}}(\alpha,\bar{\alpha}) = \frac{1}{(\alpha+\bar{\alpha})}\left\{n\,A_{n-1,\bar{n}}(\alpha,\bar{\alpha}) + \bar{n}\,A_{n,\bar{n}-1}(\alpha,\bar{\alpha}) + A_n(\alpha)A_{\bar{n}}(\bar{\alpha})\right\} \quad (2.98)$$

and, for the sake of completeness,

$$A_{o,\bar{n}}(\alpha,\bar{\alpha}) = A_{\bar{n},o}(\bar{\alpha},\alpha) = \frac{1}{(\alpha+\bar{\alpha})}\left\{\bar{n}\,A_{o,\bar{n}-1}(\alpha,\bar{\alpha}) + A_o(\alpha)A_{\bar{n}}(\bar{\alpha})\right\}$$

We now turn to the final integrals, the $\varphi_{n\bar{n}}^{ML}(\alpha,\bar{\alpha})$. We define

$$\left.\begin{aligned} f_L^m(x) &= (x^2-1)^{\frac{m}{2}} P_L^m(x) \\ g_L^m(\xi) &= (\xi^2-1)^{\frac{m}{2}} Q_L^m(\xi) \end{aligned}\right| \quad (2.99)$$

Then we may write eq. 2.54 or eq. 2.56 as

$$\begin{aligned}\varphi_{n\bar{n}}^{mL}(\alpha,\bar{\alpha}) = (-1)^m \frac{(L-m)!}{(L+m)!} \int_1^\infty d\xi \Big(& e^{-\alpha\xi}\xi^n \int_1^\xi dx\, e^{-\bar{\alpha}x} x^{\bar{n}} g_L^m(\xi) f_L^m(x) \\ & + e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^\xi dx\, e^{-\alpha x} x^n g_L^m(\;) f_L^m(x)\Big) \end{aligned} \quad (2.100)$$

Note the recursion relations[23] (K_L^m stands for P_L^m or Q_L^m)

$$\left.\begin{aligned} K_L^m(x) &= (x^2-1)^{\frac{m}{2}} \frac{d^m K_L(x)}{dx^m} \\ (2L+1)\, x\, K_L^m(x) &= (L-m+1)\, K_{L+1}^m(x) + (L+m)\, K_{L-1}^m(x) \\ (x^2-1)\frac{d K_L^m(x)}{dx} &= (L-m+1)\, K_{L+1}^m(x) - (L+1)\, x\, K_L^m(x) \end{aligned}\right| \quad (2.101)$$

We examine the identity from eqs. 2.99 and 2.101

$$\frac{d}{dx} f_L^m(x) = \frac{d}{dx}\left[(x^2-1)^{\frac{m}{2}} P_L^m(x)\right] = \frac{d}{dx}\left[(x^2-1)^m \frac{d^m P_L(x)}{dx^m}\right] \quad (2.102)$$

Performing the differentiations gives

$$m x (x^2-1)^{\frac{m}{2}-1} P_L^m(x) + (x^2-1)^{\frac{m}{2}} \frac{d P_L^m(x)}{dx} = 2mx(x^2-1)^{m-1}\frac{d^m P_L(x)}{dx} + (x^2-1)^m \frac{d^{m+1} P_L(x)}{dx^{m+1}}$$

or, in terms of the $f_L^m(x)$, we have

$$mx(x^2-1)^{-1} f_L^m(x) + (x^2-1)^{\frac{m}{2}} \frac{dP_L^m(x)}{dx} = (x^2-1)^{-1}\left[2mx f_L^m(x) + f_L^{m+1}(x)\right] \tag{2.103}$$

Then

$$f_L^{m+1}(x) = (x^2-1)^{\frac{m}{2}+1} \frac{dP_L^m(x)}{dx} - mx f_L^m(x)$$

$$= -mx f_L^m(x) + (x^2-1)^{\frac{m}{2}}\left[(L-m+1)P_{L+1}^m(x) - (L+1)x P_L^m(x)\right]$$

$$= -(L+m+1)x f_L^m(x) + (L-m+1) f_{L+1}^m(x) \tag{2.104}$$

Using the second of eqs. 2.101 we find

$$(2L+1)x f_L^m(x) = (L-m+1) f_{L+1}^m(x) + (L+m) f_{L-1}^m(x) \tag{2.105}$$

or, substituting into eq. 2.104

$$f_L^{m+1}(x) = (L-m)x f_L^m(x) - (L+m) f_{L-1}^m(x) \tag{2.106}$$

Analogous relations hold for the $g_L^m(\xi)$ due to the dual nature of the definitions and the relations 2.101. They are

$$g_L^{m+1}(\xi) = -(L+m+1)\xi g_L^m(\xi) + (L+m+1) g_{L+1}^m(\xi) \tag{2.107}$$

$$g_L^{m+1}(\xi) = (L-m)\xi g_L^m(\xi) - (L+m) g_{L-1}^m(\xi) \tag{2.108}$$

$$(2L+1)\xi g_L^m(\xi) = (L-m+1) g_{L+1}^m(\xi) + (L+m) g_{L-1}^m(\xi) \tag{2.109}$$

The following series of steps is algebraically complex. We indicate the manipulation in slightly greater detail than Rüdenberg. Multiplying eq. 2.107 by eq. 2.106 gives

$$g_L^{m+1}(\xi)f_L^{m+1}(x) = \left[(L-m+1)g_{L+1}^m(\xi) - (L+m+1)\xi g_L^m(\xi)\right]\left[-(L+m)f_{L-1}^m(x) + (L-m)xf_L^m(x)\right]$$

$$= (L-m+1)(L-m)xg_{L+1}^m(\xi)f_L^m(x) - (L-m)(L+m+1)\xi x g_L^m(\xi)f_L^m(x)$$

$$-(L-m+1)(L+m)g_{L+1}^m(\xi)f_{L-1}^m(x) + (L+m+1)(L+m)\xi g_L^m(\xi)f_{L-1}^m(x) \quad (2.110)$$

Similarly, eq. 2.108 and eq. 2.104 give

$$g_L^{m+1}(\xi)f_L^{m+1}(x) = \left[-(L+m)g_{L-1}^m(\xi) + (L-m)\xi g_L^m(\xi)\right]\left[(L-m+1)f_{L+1}^m(x) - (L+m+1)xf_L^m(x)\right]$$

$$= (L-m+1)(L-m)\xi g_L^m(\xi)f_{L+1}^m(x) - (L-m)(L+m+1)\xi x g_L^m(\xi)f_L^m(x)$$

$$-(L-m+1)(L+m)g_{L-1}^m(\xi)f_{L+1}^m(x) + (L+m+1)(L+m)xg_{L-1}^m(\xi)f_L^m(x) \quad (2.111)$$

If we now multiply eq. 2.110 by $(L+m+1)$, multiply eq. 2.111 by $(L-m)$, add, and use eq. 2.105 and eq. 2.109 to expand terms containing x(or ξ) but not ξ(or x) - i.e., $\xi g_L^m(\xi)f_{L+1}^m(x)$,etc., after collecting terms we find

$$(2L+1)g_L^{m+1}(\xi)f_L^{m+1}(x) = -(2L+1)(L+m+1)(L-m)\,x\xi g_L^m(\xi)f_L^m(x)$$

$$+(L+m+1)(L+m)^2 g_{L-1}^m(\xi)f_{L-1}^m(x)$$

$$+(L-m+1)^2(L-m)\,g_{L+1}^m(\xi)f_{L+1}^m(x) \quad (2.112)$$

We multiply eq. 2.112 by $(-1)^{m+1}\dfrac{(L-m-1)!}{(2L+1)(L+m+1)!}$ and manipulate the factorials to find

$$(-1)^{m+1}\frac{(L-[m+1])!}{(L+m+1)!}\,g_L^{m+1}(\xi)f_L^{m+1}(x) = (-1)^m\frac{(L-m)!}{(L+m)!}\,x\xi\,g_L^m(\xi)f_L^m(x)$$

$$-(-1)^m\frac{(L+m)}{(2L+1)}\left[\frac{(L-1-m)!}{(L-1+m)!}\,g_{L-1}^m(\xi)f_{L-1}^m(x)\right]$$

$$-(-1)^m\frac{(L-m+1)}{(2L+1)}\left[\frac{(L+1-m)!}{(L+1+m)!}\,g_{L+1}^m(\xi)f_{L+1}^m(x)\right] \quad (2.113)$$

Substitution of eq. 2.113 into eq. 2.100 yields immediately

$$\varphi_{n\bar{n}}^{m+1,L}(\alpha,\bar{\alpha}) = \varphi_{n+1,\bar{n}+1}^{m\,L}(\alpha,\bar{\alpha}) - \frac{(L+m)}{(2L+1)}\varphi_{n\bar{n}}^{m,L-1}(\alpha,\bar{\alpha}) - \frac{(L+1-m)}{(2L+1)}\varphi_{n\bar{n}}^{m,L+1}(\alpha,\bar{\alpha}) \quad (2.114)$$

This is the last recursion relation needed.

Before proceeding to the next section it is desirable to examine eq. 2.52 in greater detail, in particular the range of the summation over L. Again, we have

$$\left[\varphi_{kpg}^{m}\middle|\varphi_{jrs}^{m*}\right] = \frac{R^5}{8}C(m)\sum_{L=0}^{\infty}\sum_{a,b}\sum_{s,d}\delta_{Kab}\,\delta^*_{jcd}\,B_{g+b}^{mL}\,B_{s+d}^{mL}$$

$$\times\,\Phi_{p+a,r+c}^{mL}(2\alpha) \quad (2.52)$$

$$B_j^{mL} = \begin{cases}\left[\dfrac{2(2L+1)(L+m)!}{(L-m)!}\right]^{\frac{1}{2}}\dfrac{2^L j!\left(\frac{j+m+L}{2}\right)!}{\left(\frac{j+m-L}{2}\right)!\,(j+m+L+1)!} & ;\ j+m-L\geq 0 \text{ and even}\\ 0 \text{ otherwise}\end{cases}$$

Aquick check of Appendix I shows that the δ,δ^*_{ab} matrices are finite and square in the indices a and b. Let us denote the dimensions of δ_{Kab} and δ^*_{Kab} as $max(k)$ and $max^*(k)$ respectively. Note that $max(k)+2 = max^*(k)$. Since the B_j^{mL} vanish for $L > j+m$, we see that the maximum value of L will be the smaller of $g+b+m$ and $s+d+m$. This suggests that the summations on L be performed inside the other summations. We also have the further restriction that $L \geq m$. Hence we write

$$\left[\varphi^m_{kpg} \middle| \varphi^{m*}_{jrs}\right] = \frac{R^5}{8} C(m) \sum_{a,b=0}^{max(k)+1} \sum_{c,d=0}^{max(j)+1} \sum_{L=m}^{L\,max} \delta_{kab}\, \delta^*_{jcd}\, B^{mL}_{g+b}\, B^{mL}_{s+d}$$

$$\times\, \Phi^{mL}_{p+a,r+c}(2\alpha) \qquad (2.52^*)$$

where

$$L\,max = \text{smaller of} \begin{cases} g+b+m \\ s+d+m \end{cases}$$

$max(k)$ is the dimension of δ_{kab} in a and b.

Hence the sums have been reduced to finite range.

IV - Computer programs for the electronic integrals

We now turn to the problem of programming the expressions of sections I and II. We present flowcharts of the computation in three parts - 1) the control program (Appendix 2), 2) the recursion programs for the auxiliary functions (Appendix 3), and 3) the computation of the Lamb term, including the integrals defined by eqs. 2.7, 2.9, and 2.10. Equation numbers are given on the flowcharts as reference to the text.

The control program reads in the orbital exponents arranged in the same order as the sets of wave functions to be read by the Lamb term program. It then calls on the other programs in turn and supplies the necessary parameters.

The program for the recursions uses two parameters as input supplied by the control. For our particular case these two parameters will be identical in value and equal to twice the orbital exponent for the particular wave function being used. The sizes of the arrays to be generated are extremely large, and the program will require some sophisticated data storage and handling in practice. As written in the appendix, the program will compute all $\varphi_{n\bar{n}}^{ML}(\alpha,\bar{\alpha})$ for M=0(1)2, L=0(1)13, and $n,\bar{n}$=0(1)16 as required by Kolos and Roothaan's 50-term functions. 'Infinite' storage is assumed.

The Lamb term program reads the wave function coefficients and exponents, reads the output of the recursion program, and computes the diamagnetic shielding by assembling functions of functions, etc. in such a way that the program may easily be modified to compute any expectation values expressible in terms of the K_{pqrs}^{μ}, $\langle \varphi_{kpq}^{m} | \varphi_{jrs}^{m*} \rangle$, or $[\varphi_{kpq}^{m} | \varphi_{jrs}^{m*}]$ integrals.

V - Appendices

Appendix I - the coefficients δ_{kab} and δ^*_{kab} from eqs. 2.8 and 2.25

δ_{kab}

k=1 $\delta_{00}=1$

k=2

a\b	0	1	2
0	-1	0	1
1	0	0	0
2	1	0	0

k=3

a\b	0	1	2	3	4
0	1	0	-2	0	1
1	0	0	0	0	0
2	-2	0	2	0	0
3	0	0	0	0	0
4	1	0	0	0	0

k=4

a\b	0	1	2
0	0	0	0
1	0	0	0
2	0	0	1

k=5

a\b	0	1	2
0	-1	0	1
1	0	0	0
2	1	0	-1

k=6

a\b	0	1
0	0	0
1	0	1

k=7

a\b	0	1	2	3
0	0	0	0	0
1	0	-1	0	1
2	0	0	0	0
3	0	1	0	-1

NOTE:
$\delta_{kab} = \delta_{kba}$

$\underline{\delta^*_{kab}}$

$\underline{k=1}$

a \ b	0	1	2
0	0	0	-1
1	0	0	0
2	1	0	0

$\underline{k=2}$

a \ b					
	0	0	1	0	-1
	0	0	0	0	0
	-1	0	0	0	0
	0	0	0	0	0
	1	0	0	0	0

$\underline{k=3}$

a \ b	0	1	2	3	4	5	6
0	0	0	0	0	1	0	-1
1	0	0	0	0	0	0	0
2	0	0	0	0	-1	0	0
3	0	0	0	0	0	0	0
4	-1	0	1	0	0	0	0
5	0	0	0	0	0	0	0
6	1	0	0	0	0	0	0

$\underline{k=4}$

a \ b	0	1	2	3	4
0	0	0	0	0	0
1	0	0	0	0	0
2	0	0	0	0	-1
3	0	0	0	0	0
4	0	0	1	0	0

$\underline{k=5}$

a \ b	0	1	2	3	4
0	0	0	1	0	-1
1	0	0	0	0	0
2	-1	0	0	0	1
3	0	0	0	0	0
4	1	0	-1	0	0

$\underline{k=6}$

a \ b	0	1	2	3
0	0	0	0	0
1	0	0	0	-1
2	0	0	0	0
3	0	1	0	0

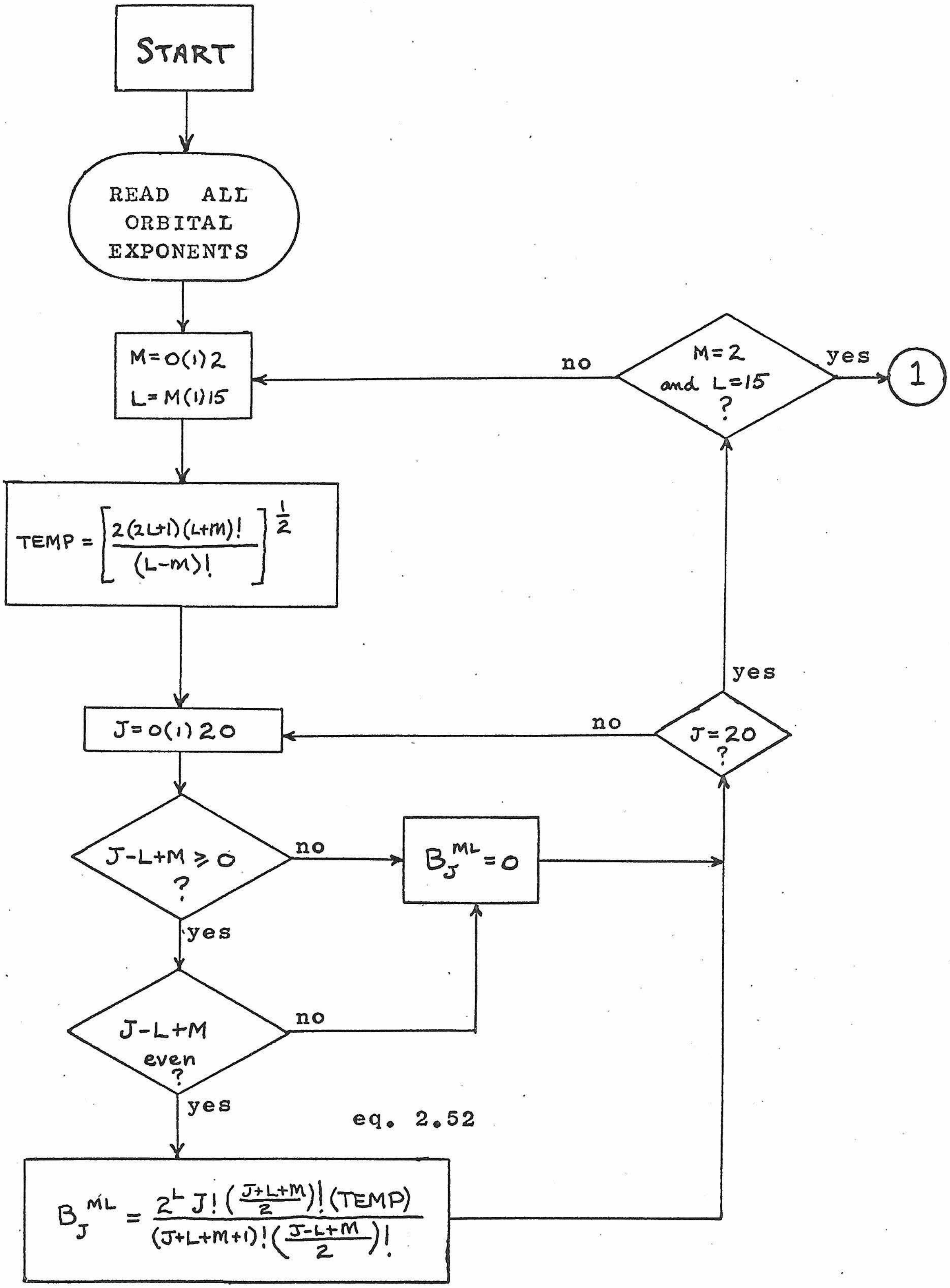
$\underline{k=7}$

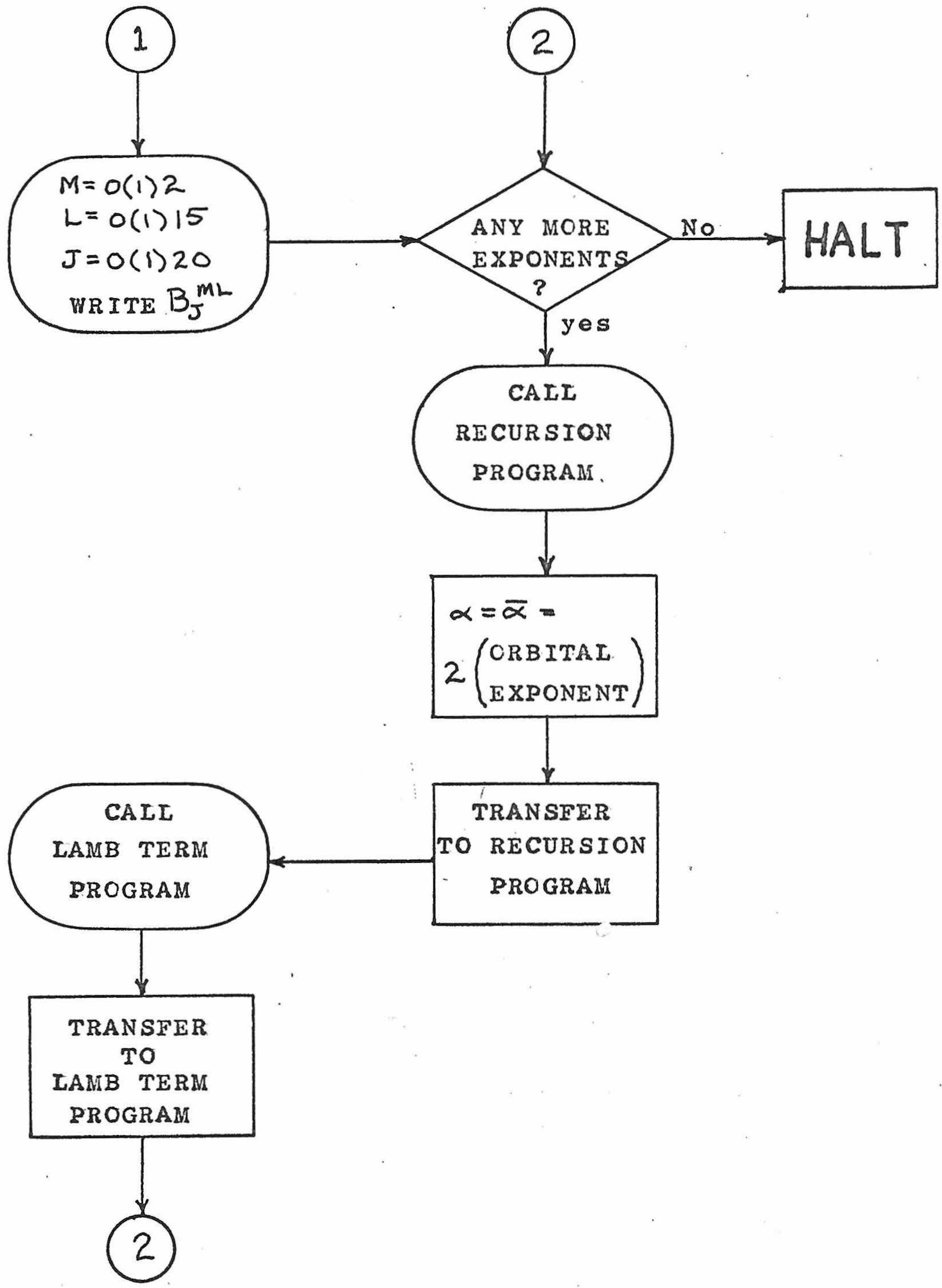
a \ b	0	1	2	3	4	5
0	0	0	0	0	0	0
1	0	0	0	1	0	-1
2	0	0	0	0	0	0
3	0	-1	0	0	0	0
4	0	0	0	0	0	0
5	0	1	0	0	0	0

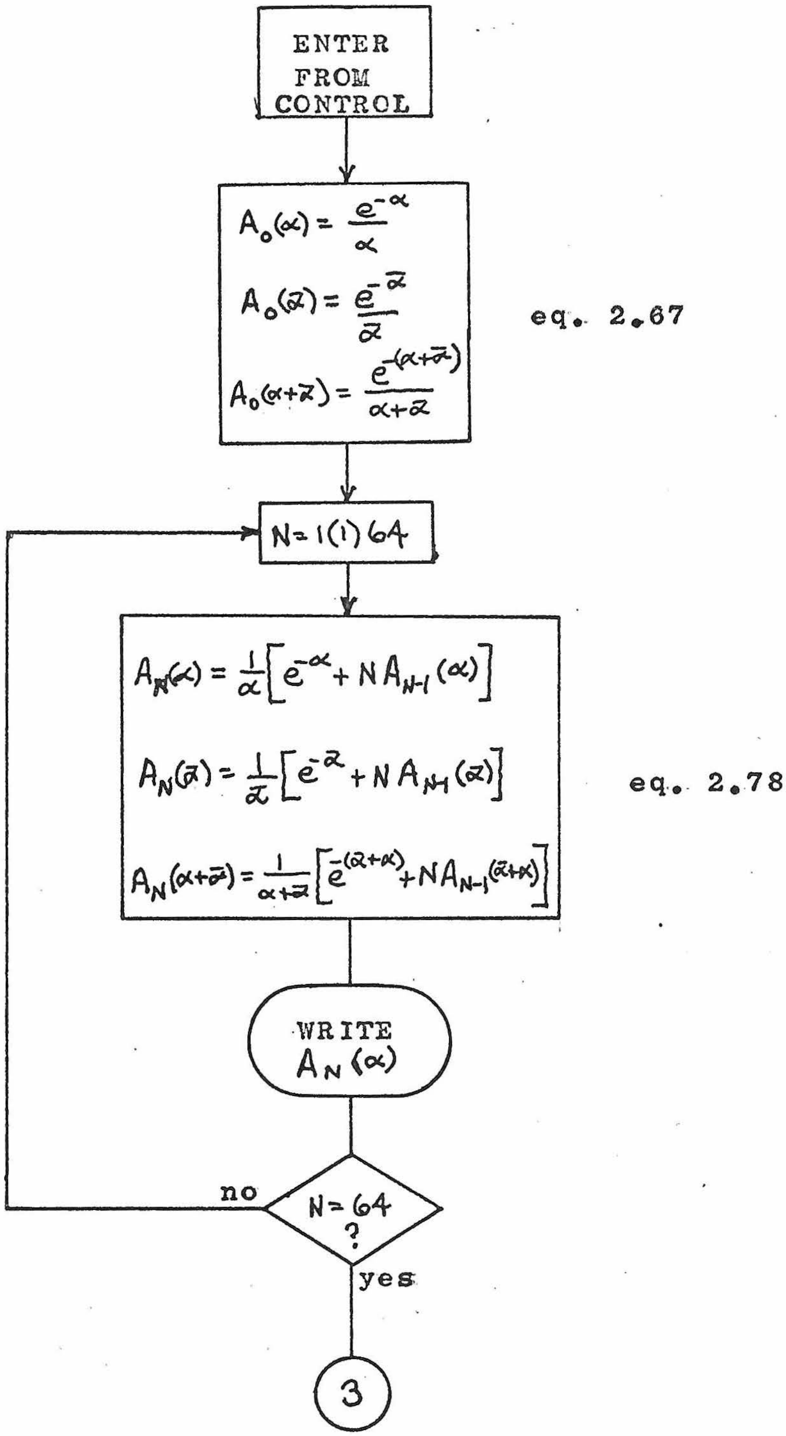
NOTE:

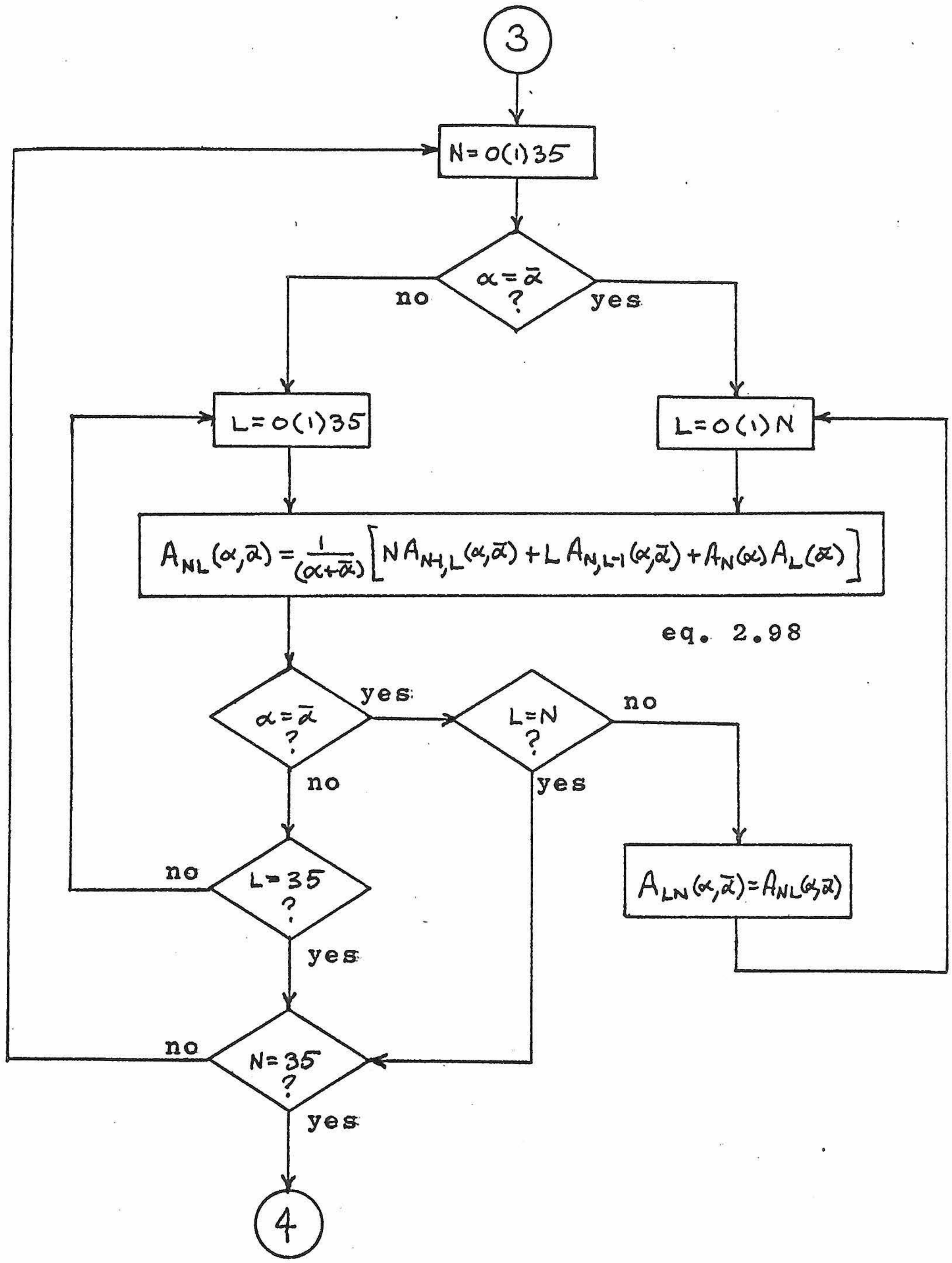
$$\delta^*_{kab} = -\delta^*_{kba}$$

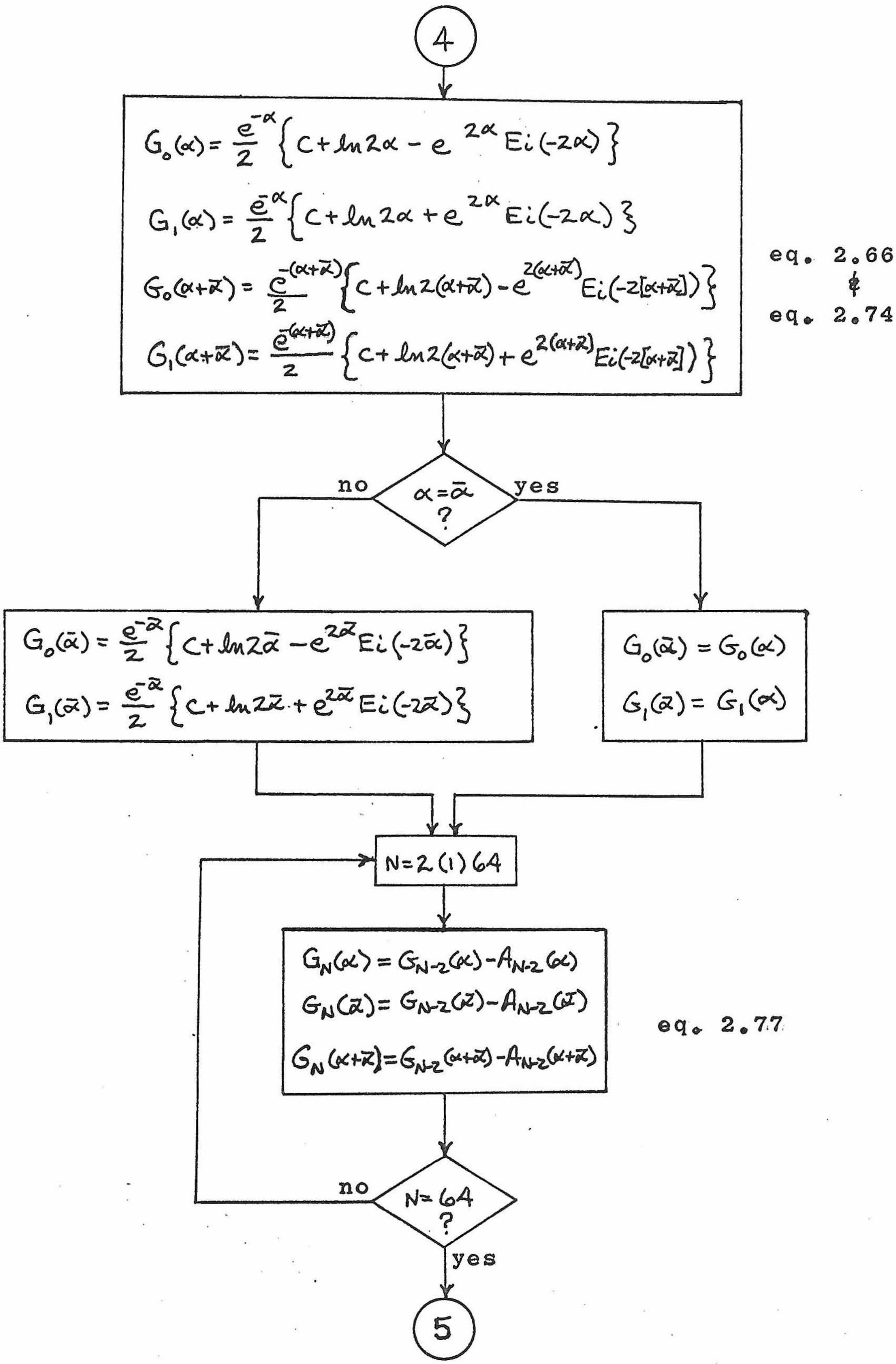
Appendix 2 - The control program



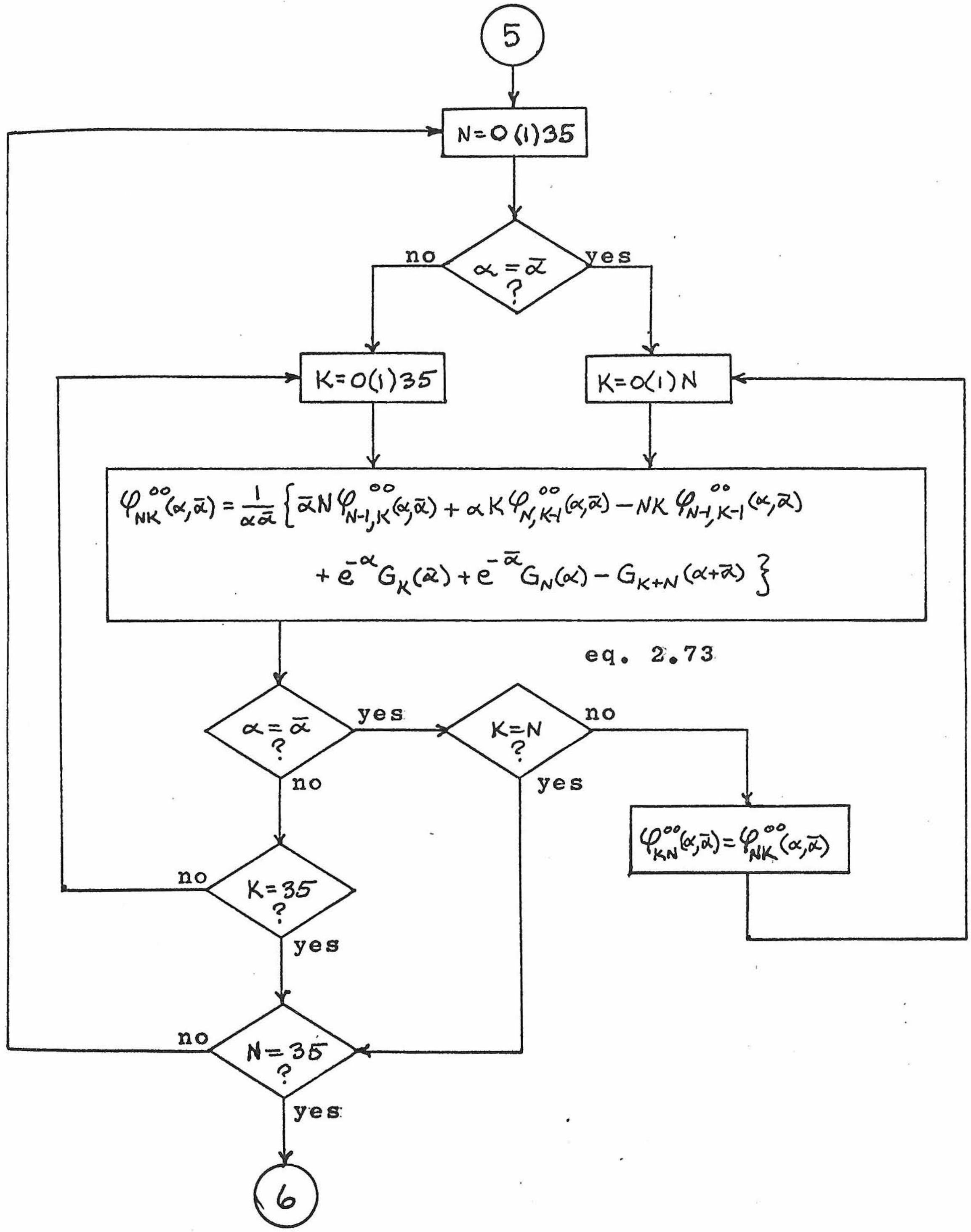

1
2
M=0(1)2
L=0(1)15
J=0(1)20
WRITE B_J^{ML}
ANY MORE EXPONENTS ?
No
HALT
yes
CALL RECURSION PROGRAM.
$\alpha = \bar{\alpha} =$ 2 (ORBITAL EXPONENT)
TRANSFER TO RECURSION PROGRAM
CALL LAMB TERM PROGRAM
TRANSFER TO LAMB TERM PROGRAM
2

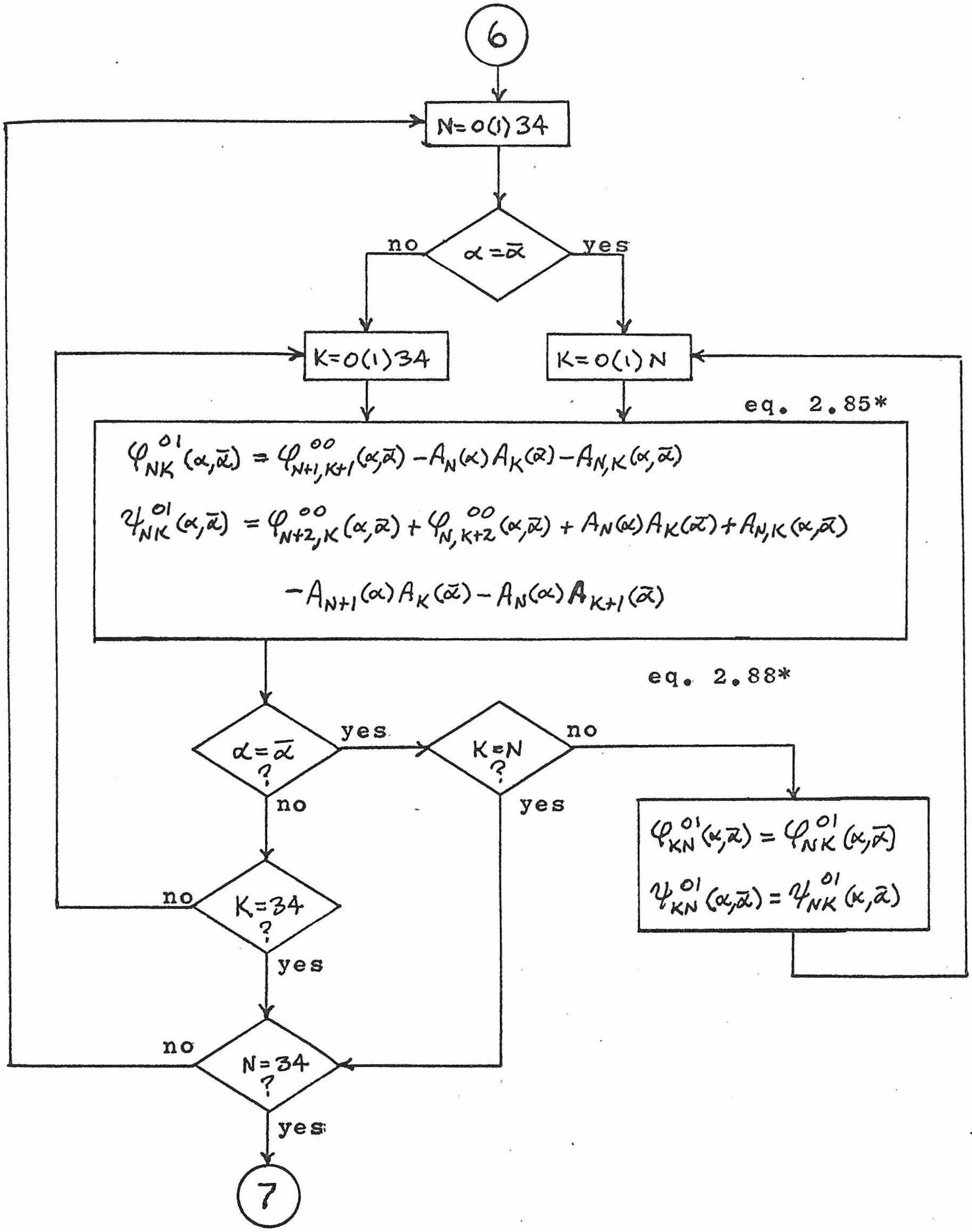

ENTER FROM CONTROL
$A_0(\alpha) = \frac{e^{-\alpha}}{\alpha}$
$A_0(\bar{\alpha}) = \frac{e^{-\bar{\alpha}}}{\bar{\alpha}}$
$A_0(\alpha+\bar{\alpha}) = \frac{e^{-(\alpha+\bar{\alpha})}}{\alpha+\bar{\alpha}}$
eq. 2.67
N=1(1)64
$A_N(\alpha) = \frac{1}{\alpha}\left[e^{-\alpha} + N A_{N-1}(\alpha)\right]$
$A_N(\bar{\alpha}) = \frac{1}{\bar{\alpha}}\left[e^{-\bar{\alpha}} + N A_{N-1}(\bar{\alpha})\right]$
$A_N(\alpha+\bar{\alpha}) = \frac{1}{\alpha+\bar{\alpha}}\left[e^{-(\bar{\alpha}+\alpha)} + N A_{N-1}(\bar{\alpha}+\alpha)\right]$
eq. 2.78
WRITE $A_N(\alpha)$
N=64 ?
no
yes
3

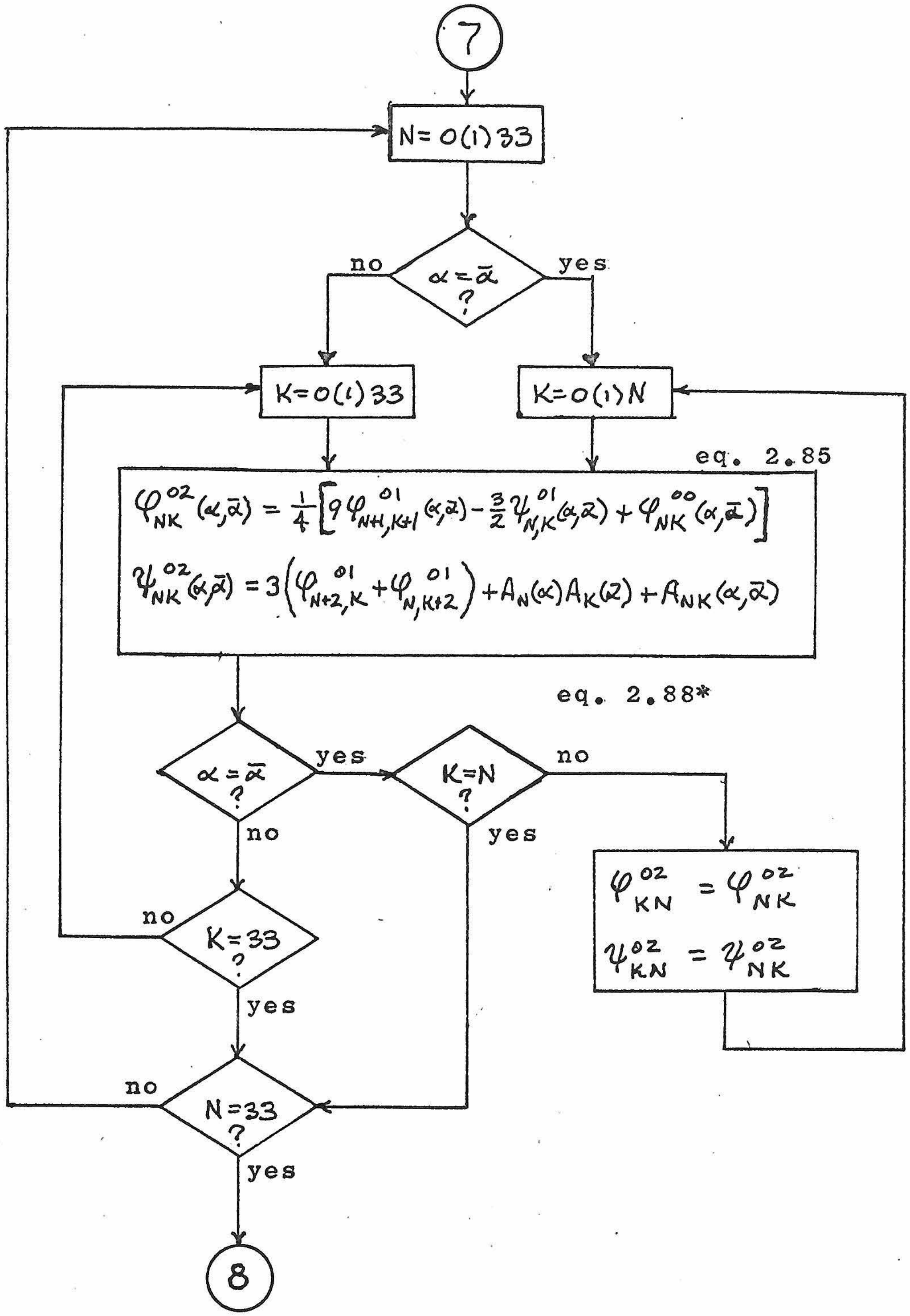

3
N=0(1)35
α=ᾱ ?
no
yes
L=0(1)35
L=0(1)N
$A_{NL}(\alpha,\bar\alpha) = \frac{1}{(\alpha+\bar\alpha)}\left[N A_{N-1,L}(\alpha,\bar\alpha) + L A_{N,L-1}(\alpha,\bar\alpha) + A_N(\alpha) A_L(\bar\alpha)\right]$
eq. 2.98
α=ᾱ ?
yes
no
L=N ?
no
yes
no
L=35 ?
yes
$A_{LN}(\alpha,\bar\alpha)=A_{NL}(\alpha,\bar\alpha)$
no
N=35 ?
yes
4

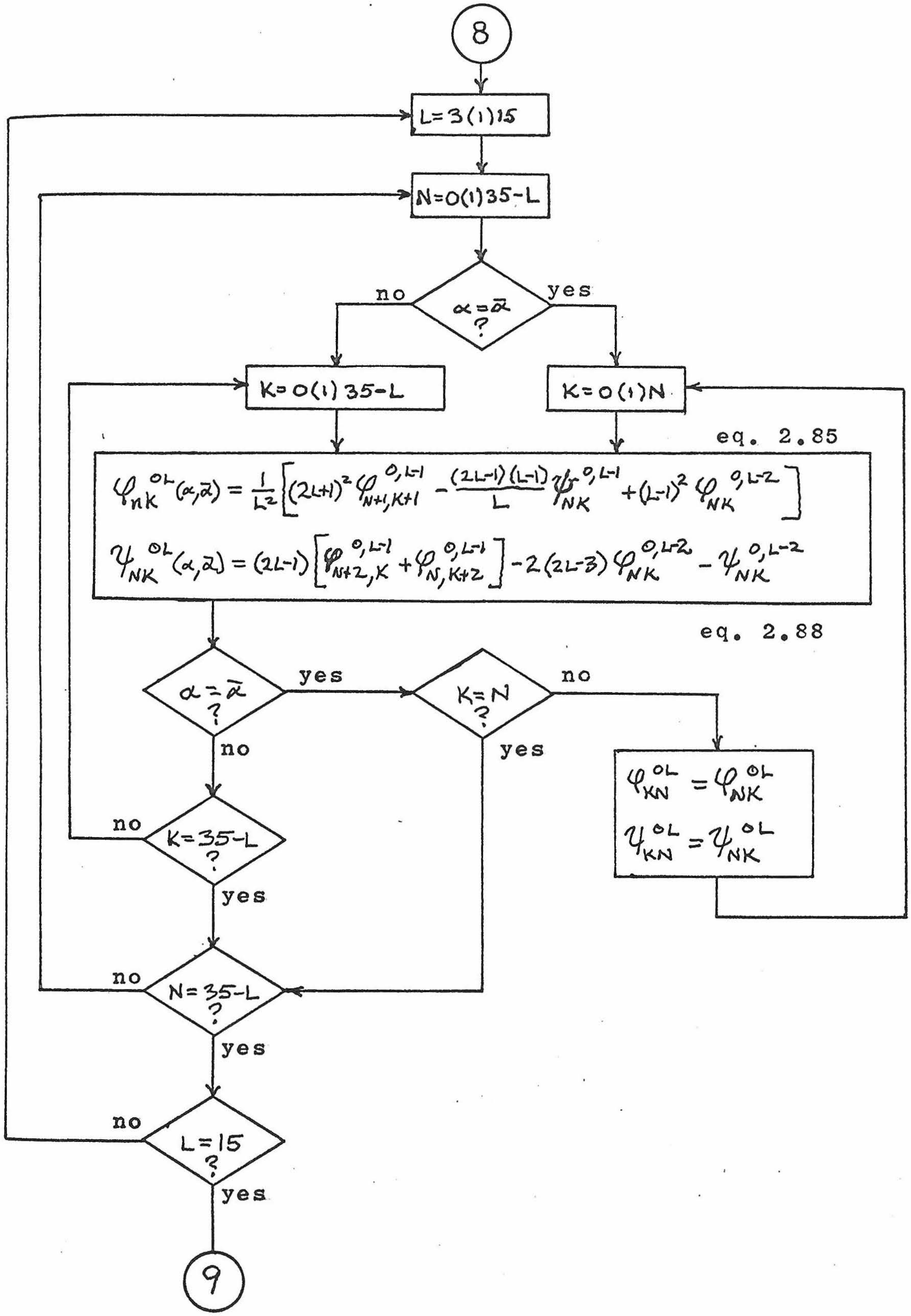


4
$G_0(\alpha) = \frac{e^{-\alpha}}{2}\left\{C + \ln 2\alpha - e^{2\alpha}\,Ei(-2\alpha)\right\}$
$G_1(\alpha) = \frac{e^{-\alpha}}{2}\left\{C + \ln 2\alpha + e^{2\alpha}\,Ei(-2\alpha)\right\}$
$G_0(\alpha+\bar{\alpha}) = \frac{e^{-(\alpha+\bar{\alpha})}}{2}\left\{C + \ln 2(\alpha+\bar{\alpha}) - e^{2(\alpha+\bar{\alpha})}\,Ei(-2[\alpha+\bar{\alpha}])\right\}$
$G_1(\alpha+\bar{\alpha}) = \frac{e^{-(\alpha+\bar{\alpha})}}{2}\left\{C + \ln 2(\alpha+\bar{\alpha}) + e^{2(\alpha+\bar{\alpha})}\,Ei(-2[\alpha+\bar{\alpha}])\right\}$
eq. 2.66
&
eq. 2.74
no
$\alpha = \bar{\alpha}$?
yes
$G_0(\bar{\alpha}) = \frac{e^{-\bar{\alpha}}}{2}\left\{C + \ln 2\bar{\alpha} - e^{2\bar{\alpha}}\,Ei(-2\bar{\alpha})\right\}$
$G_1(\bar{\alpha}) = \frac{e^{-\bar{\alpha}}}{2}\left\{C + \ln 2\bar{\alpha} + e^{2\bar{\alpha}}\,Ei(-2\bar{\alpha})\right\}$
$G_0(\bar{\alpha}) = G_0(\alpha)$
$G_1(\bar{\alpha}) = G_1(\alpha)$
$N = 2(1)64$
$G_N(\alpha) = G_{N-2}(\alpha) - A_{N-2}(\alpha)$
$G_N(\bar{\alpha}) = G_{N-2}(\bar{\alpha}) - A_{N-2}(\bar{\alpha})$
$G_N(\alpha+\bar{\alpha}) = G_{N-2}(\alpha+\bar{\alpha}) - A_{N-2}(\alpha+\bar{\alpha})$
eq. 2.77
no
$N = 64$?
yes
5

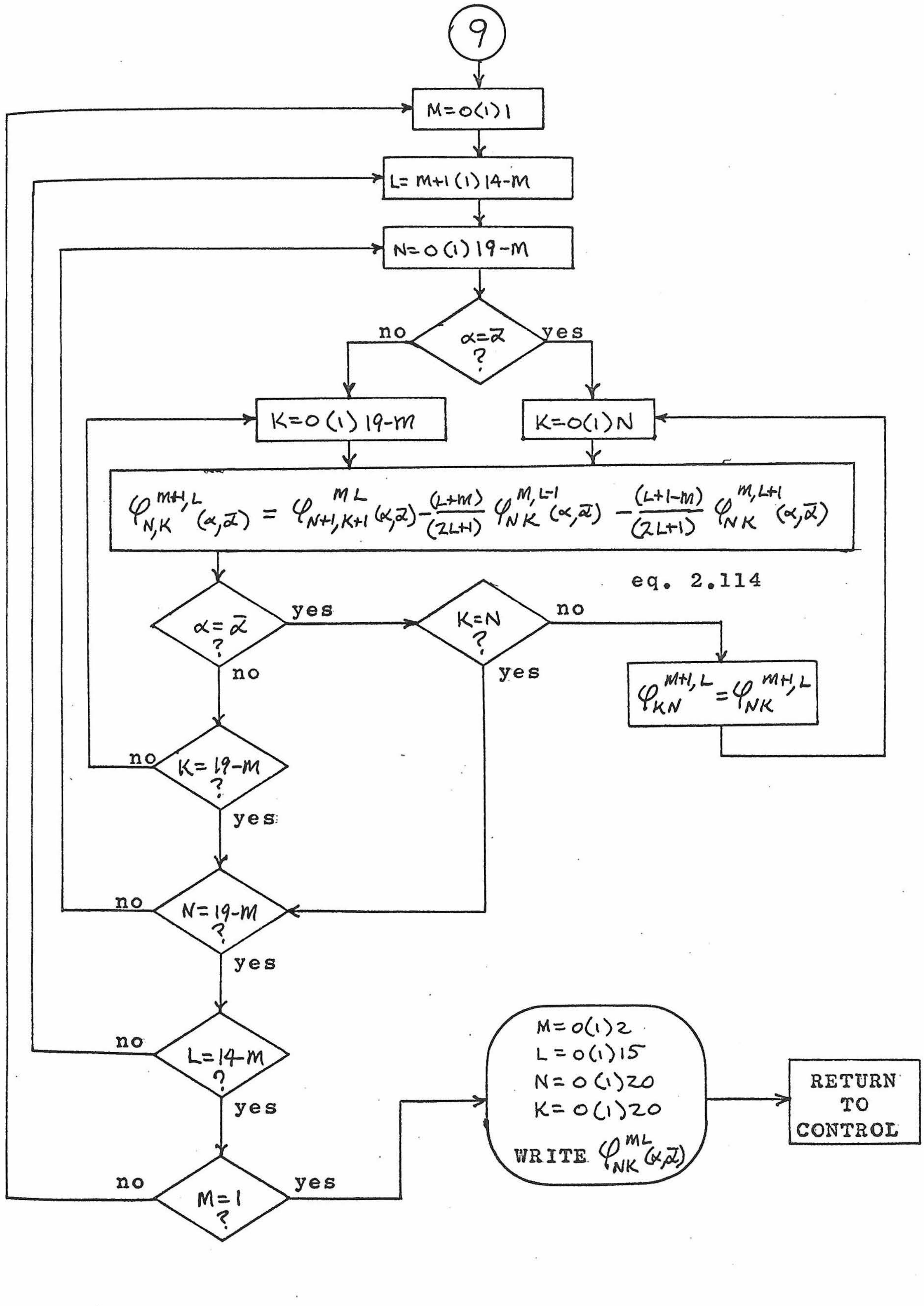

5
N=0(1)35
no
$\alpha = \bar{\alpha}$?
yes
K=0(1)35
K=α(1)N
$\varphi^{00}_{NK}(\alpha,\bar{\alpha}) = \frac{1}{\alpha\bar{\alpha}}\Big\{\bar{\alpha}N\varphi^{00}_{N-1,K}(\alpha,\bar{\alpha}) + \alpha K\varphi^{00}_{N,K-1}(\alpha,\bar{\alpha}) - NK\varphi^{00}_{N-1,K-1}(\alpha,\bar{\alpha})$
$+ e^{-\alpha}G_K(\bar{\alpha}) + e^{-\bar{\alpha}}G_N(\alpha) - G_{K+N}(\alpha+\bar{\alpha})\Big\}$
eq. 2.73
$\alpha = \bar{\alpha}$?
yes
no
K=N ?
no
yes
$\varphi^{00}_{KN}(\alpha,\bar{\alpha}) = \varphi^{00}_{NK}(\alpha,\bar{\alpha})$
no
K=35 ?
yes
no
N=35 ?
yes
6


6
N=0(1)34
$\alpha=\bar{\alpha}$
no
yes
K=0(1)34
K=0(1)N
eq. 2.85*
$\varphi^{01}_{NK}(\alpha,\bar{\alpha}) = \varphi^{00}_{N+1,K+1}(\alpha,\bar{\alpha}) - A_N(\alpha)A_K(\bar{\alpha}) - A_{N,K}(\alpha,\bar{\alpha})$
$\psi^{01}_{NK}(\alpha,\bar{\alpha}) = \varphi^{00}_{N+2,K}(\alpha,\bar{\alpha}) + \varphi^{00}_{N,K+2}(\alpha,\bar{\alpha}) + A_N(\alpha)A_K(\bar{\alpha}) + A_{N,K}(\alpha,\bar{\alpha}) - A_{N+1}(\alpha)A_K(\bar{\alpha}) - A_N(\alpha)A_{K+1}(\bar{\alpha})$
eq. 2.88*
$\alpha=\bar{\alpha}$?
yes
no
K=N ?
no
yes
$\varphi^{01}_{KN}(\alpha,\bar{\alpha}) = \varphi^{01}_{NK}(\alpha,\bar{\alpha})$
$\psi^{01}_{KN}(\alpha,\bar{\alpha}) = \psi^{01}_{NK}(\alpha,\bar{\alpha})$
no
K=34 ?
yes
no
N=34 ?
yes
7

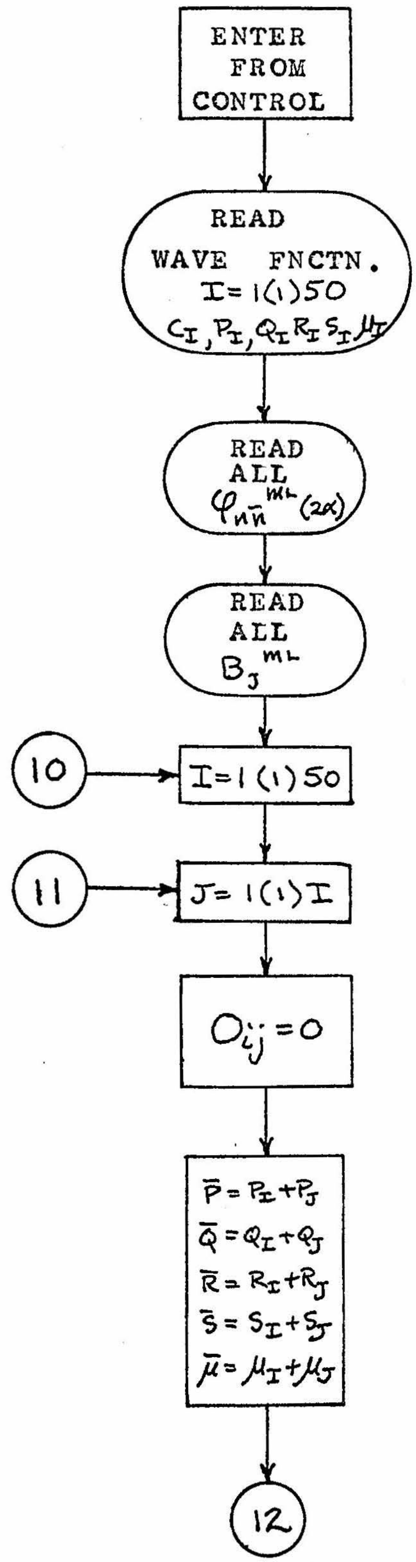

7
N = 0(1)33
α = ᾱ ?
no
yes
K = 0(1)33
K = 0(1)N
eq. 2.85
$\varphi^{02}_{NK}(\alpha,\bar\alpha) = \frac{1}{4}\left[9\varphi^{01}_{N+1,K+1}(\alpha,\bar\alpha) - \frac{3}{2}\psi^{01}_{N,K}(\alpha,\bar\alpha) + \varphi^{00}_{NK}(\alpha,\bar\alpha)\right]$
$\psi^{02}_{NK}(\alpha,\bar\alpha) = 3\left(\varphi^{01}_{N+2,K} + \varphi^{01}_{N,K+2}\right) + A_N(\alpha)A_K(\bar\alpha) + A_{NK}(\alpha,\bar\alpha)$
eq. 2.88*
α = ᾱ ?
yes
no
K = N ?
no
yes
$\varphi^{02}_{KN} = \varphi^{02}_{NK}$
$\psi^{02}_{KN} = \psi^{02}_{NK}$
K = 33 ?
no
yes
N = 33 ?
no
yes
8

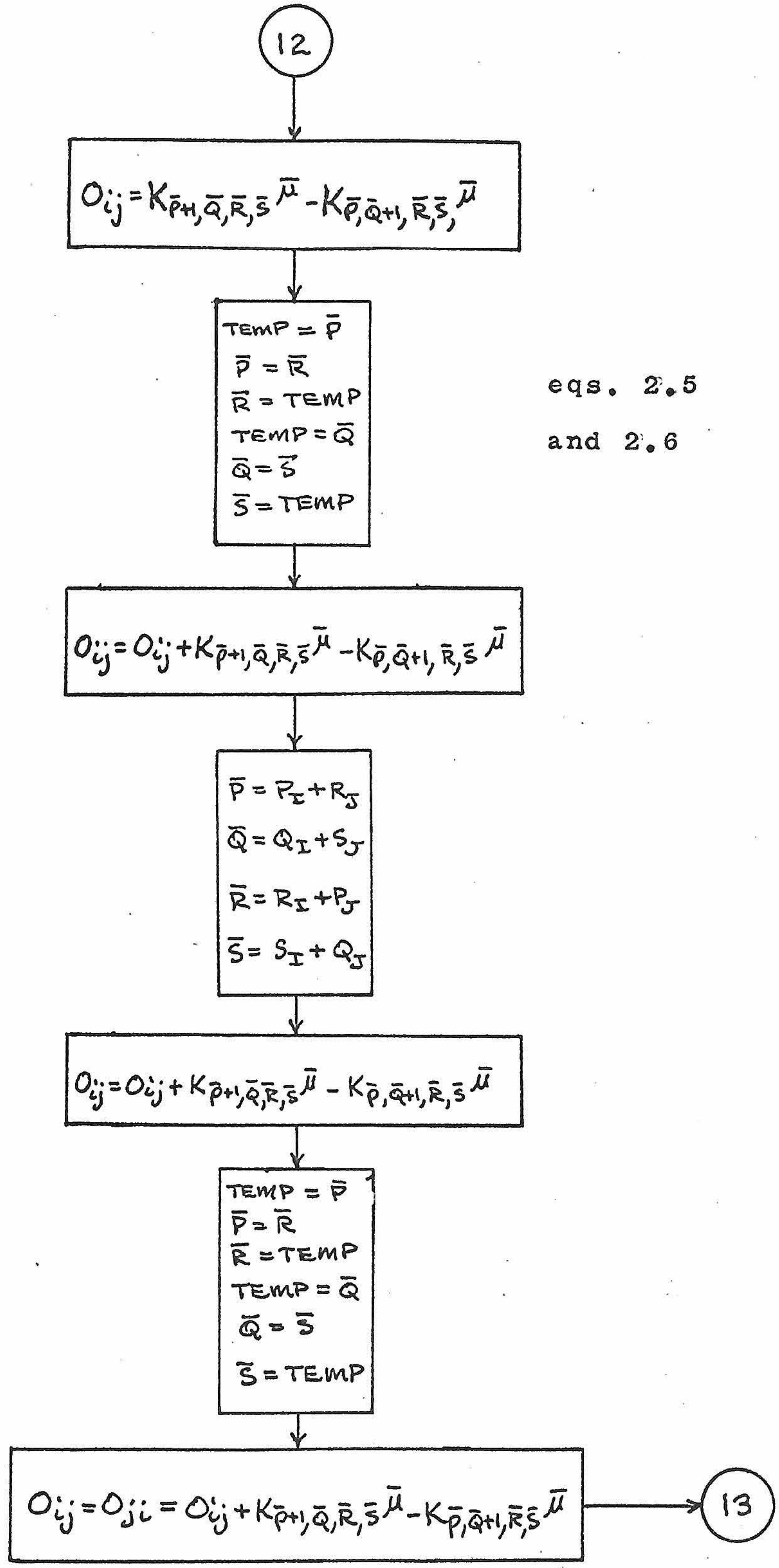


8
L=3(1)15
N=0(1)35-L
α=ᾱ ?
no
yes
K=0(1)35-L
K=0(1)N
eq. 2.85
$\varphi_{NK}^{0L}(\alpha,\bar{\alpha}) = \frac{1}{L^2}\left[(2L+1)^2\varphi_{N+1,K+1}^{0,L-1} - \frac{(2L-1)(L-1)}{L}\psi_{NK}^{0,L-1} + (L-1)^2\varphi_{NK}^{0,L-2}\right]$
$\psi_{NK}^{0L}(\alpha,\bar{\alpha}) = (2L-1)\left[\varphi_{N+2,K}^{0,L-1} + \varphi_{N,K+2}^{0,L-1}\right] - 2(2L-3)\varphi_{NK}^{0,L-2} - \psi_{NK}^{0,L-2}$
eq. 2.88
α=ᾱ ?
yes
no
K=N ?
no
yes
$\varphi_{KN}^{0L} = \varphi_{NK}^{0L}$
$\psi_{KN}^{0L} = \psi_{NK}^{0L}$
no
K=35-L ?
yes
no
N=35-L ?
yes
no
L=15 ?
yes
9


9
M=0(1)1
L= M+1 (1) 14-M
N=0 (1) 19-M
α=ᾱ ?
no
yes
K=0 (1) 19-M
K=0(1)N
$\varphi^{M+1,L}_{N,K}(\alpha,\bar\alpha) = \varphi^{ML}_{N+1,K+1}(\alpha,\bar\alpha) - \frac{(L+M)}{(2L+1)}\varphi^{M,L-1}_{NK}(\alpha,\bar\alpha) - \frac{(L+1-M)}{(2L+1)}\varphi^{M,L+1}_{NK}(\alpha,\bar\alpha)$
eq. 2.114
α=ᾱ ?
yes
no
K=N ?
no
yes
$\varphi^{M+1,L}_{KN} = \varphi^{M+1,L}_{NK}$
K= 19-M ?
no
yes
N= 19-M ?
no
yes
L=14-M ?
no
yes
M=1 ?
no
yes
M=0(1)2
L=0(1)15
N=0(1)20
K=0(1)20
WRITE $\varphi^{ML}_{NK}(\alpha,\bar\alpha)$
RETURN TO CONTROL

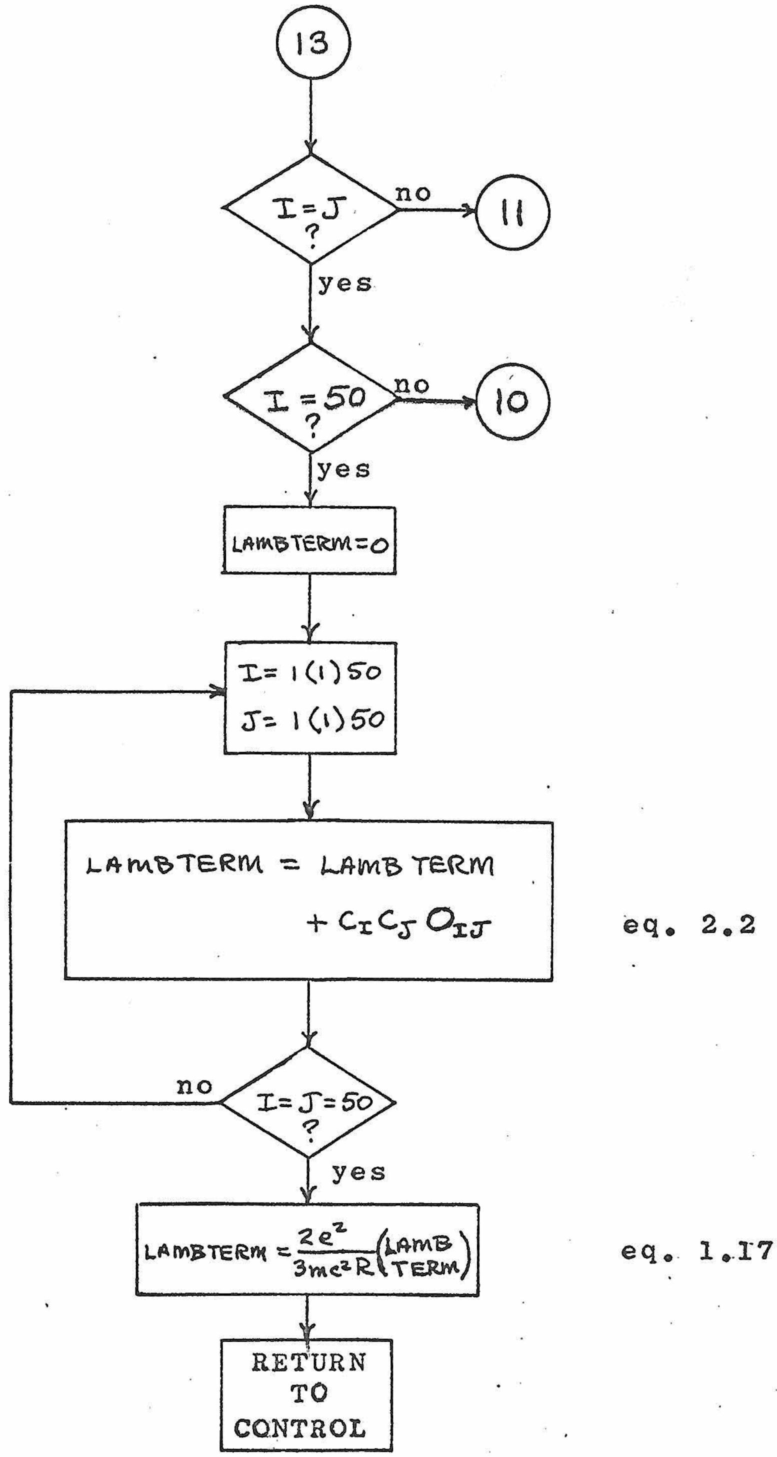
Appendix IV - Diamagnetic shielding program



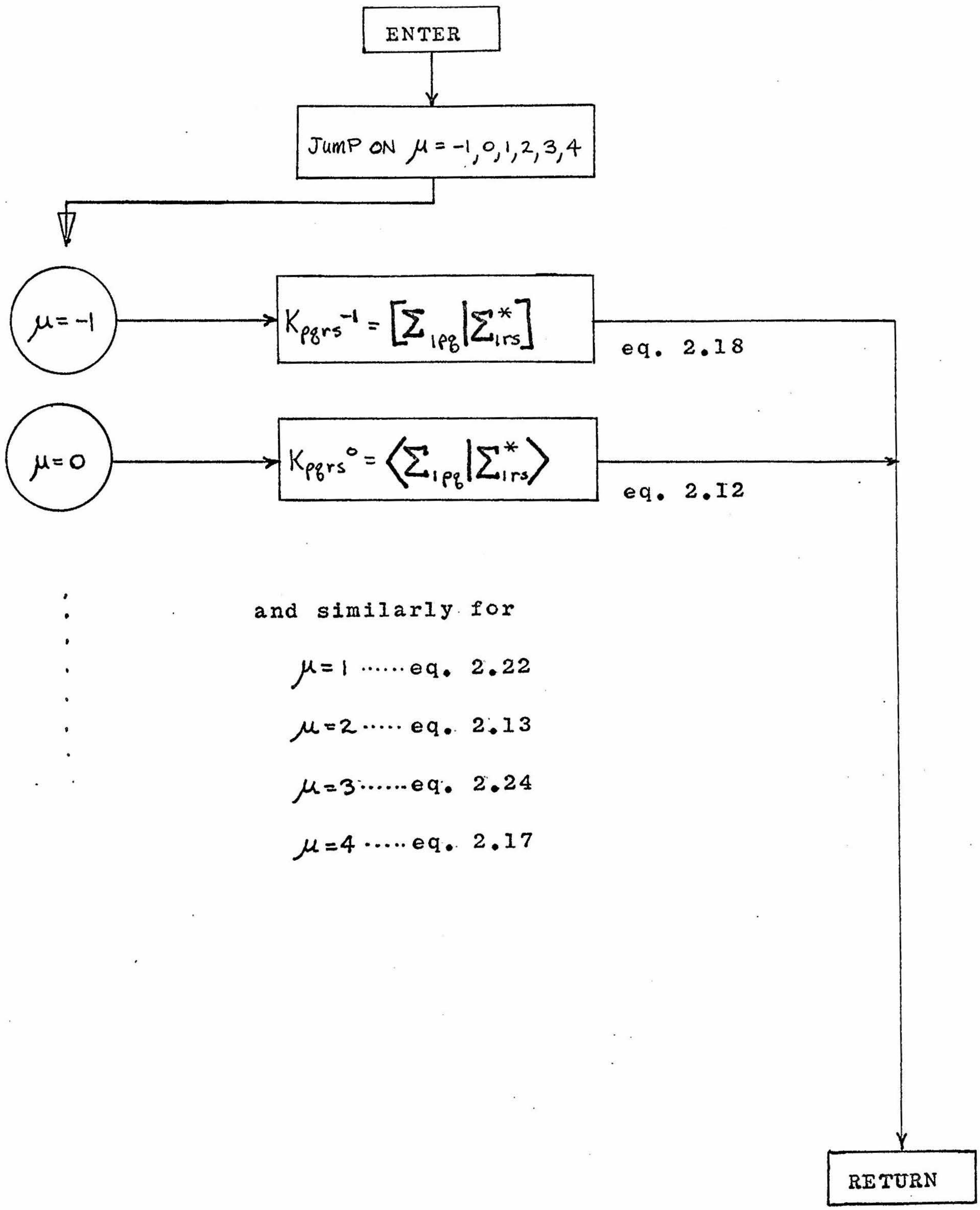

12
$O_{ij} = K_{\bar{P}+1,\bar{Q},\bar{R},\bar{S}}{}^{\bar{\mu}} - K_{\bar{P},\bar{Q}+1,\bar{R},\bar{S}}{}^{\bar{\mu}}$
TEMP = $\bar{P}$
$\bar{P} = \bar{R}$
$\bar{R}$ = TEMP
TEMP = $\bar{Q}$
$\bar{Q} = \bar{S}$
$\bar{S}$ = TEMP
$O_{ij} = O_{ij} + K_{\bar{P}+1,\bar{Q},\bar{R},\bar{S}}{}^{\bar{\mu}} - K_{\bar{P},\bar{Q}+1,\bar{R},\bar{S}}{}^{\bar{\mu}}$
$\bar{P} = P_I + R_J$
$\bar{Q} = Q_I + S_J$
$\bar{R} = R_I + P_J$
$\bar{S} = S_I + Q_J$
$O_{ij} = O_{ij} + K_{\bar{P}+1,\bar{Q},\bar{R},\bar{S}}{}^{\bar{\mu}} - K_{\bar{P},\bar{Q}+1,\bar{R},\bar{S}}{}^{\bar{\mu}}$
TEMP = $\bar{P}$
$\bar{P} = \bar{R}$
$\bar{R}$ = TEMP
TEMP = $\bar{Q}$
$\bar{Q} = \bar{S}$
$\bar{S}$ = TEMP
$O_{ij} = O_{ji} = O_{ij} + K_{\bar{P}+1,\bar{Q},\bar{R},\bar{S}}{}^{\bar{\mu}} - K_{\bar{P},\bar{Q}+1,\bar{R},\bar{S}}{}^{\bar{\mu}}$
13

eqs. 2.5

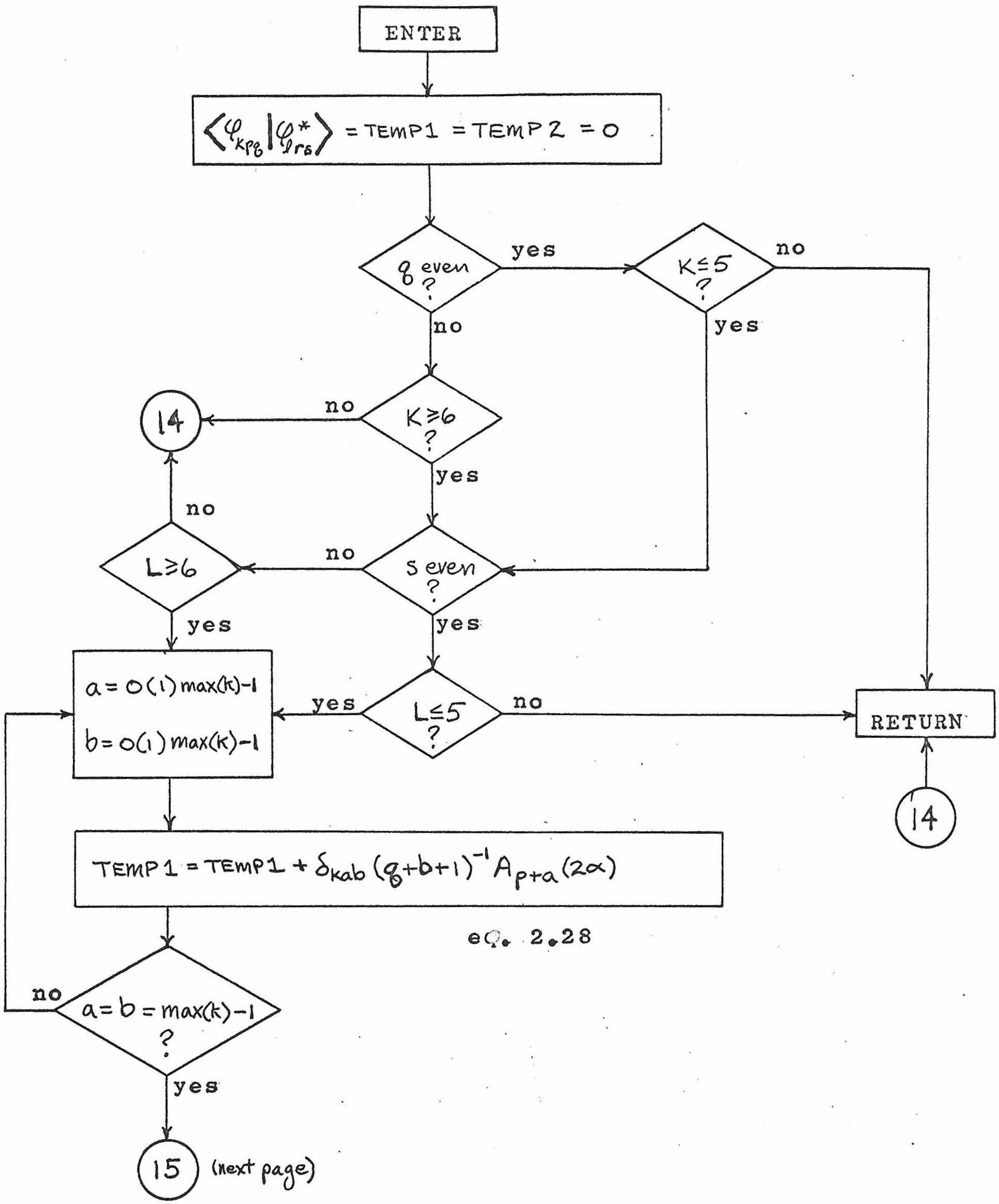
and 2.6

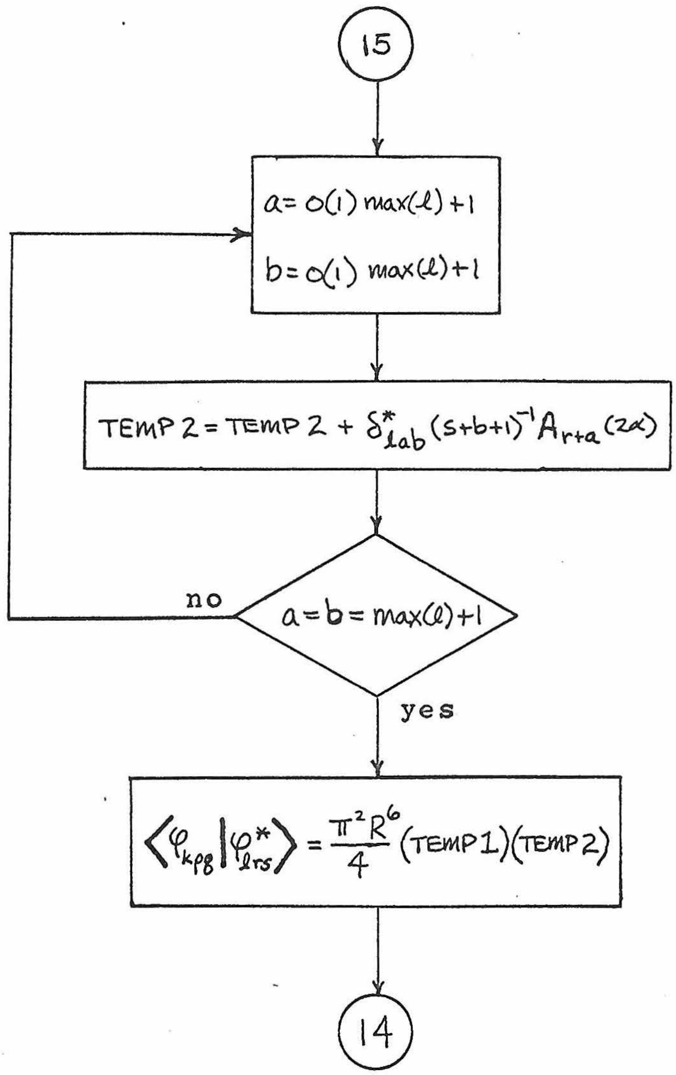

13
I=J ?
no
11
yes
I=50 ?
no
10
yes
LAMBTERM=0
I= 1(1)50
J= 1(1)50
LAMBTERM = LAMBTERM + C_I C_J O_IJ
eq. 2.2
no
I=J=50 ?
yes
LAMBTERM = 2e^2/(3mc^2 R) (LAMB TERM)
eq. 1.17
RETURN TO CONTROL

The functions K_{pqrs}^{μ}



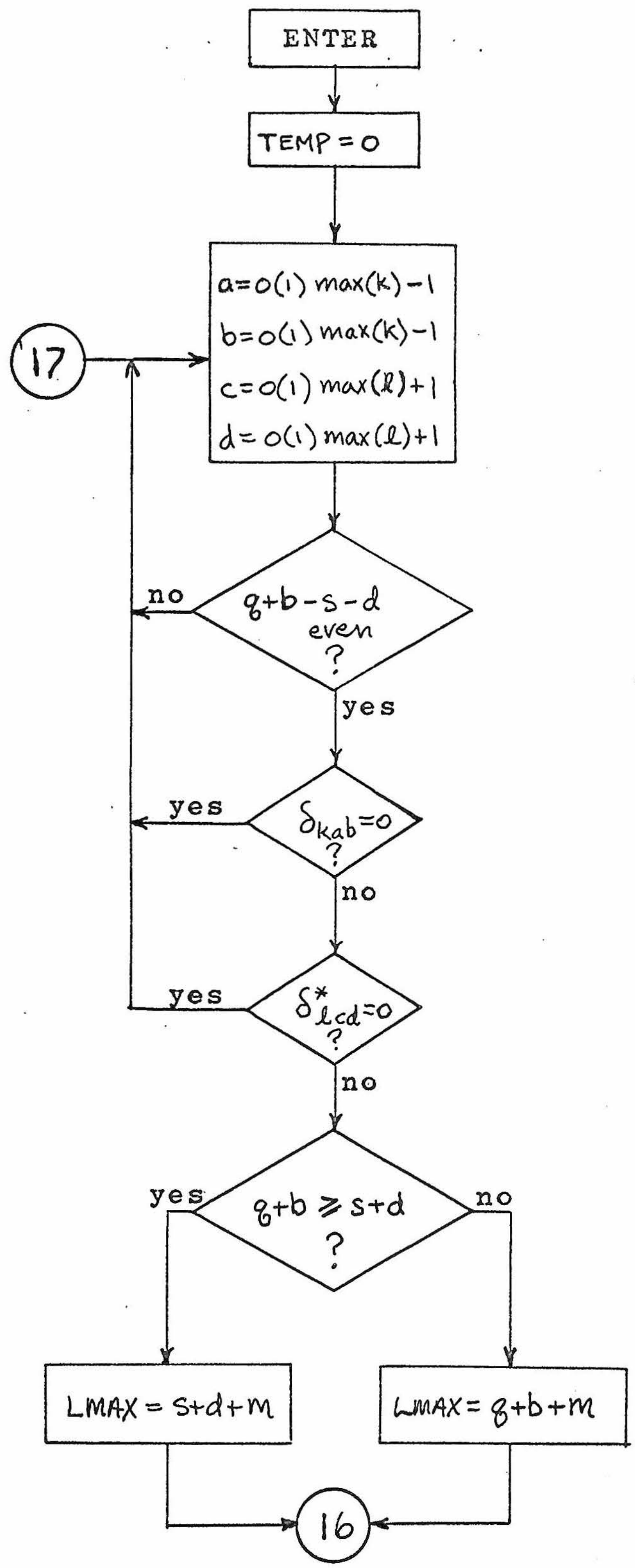
The functions $\left\langle \varphi_{Kpq} \middle| \varphi^*_{Lrs} \right\rangle$

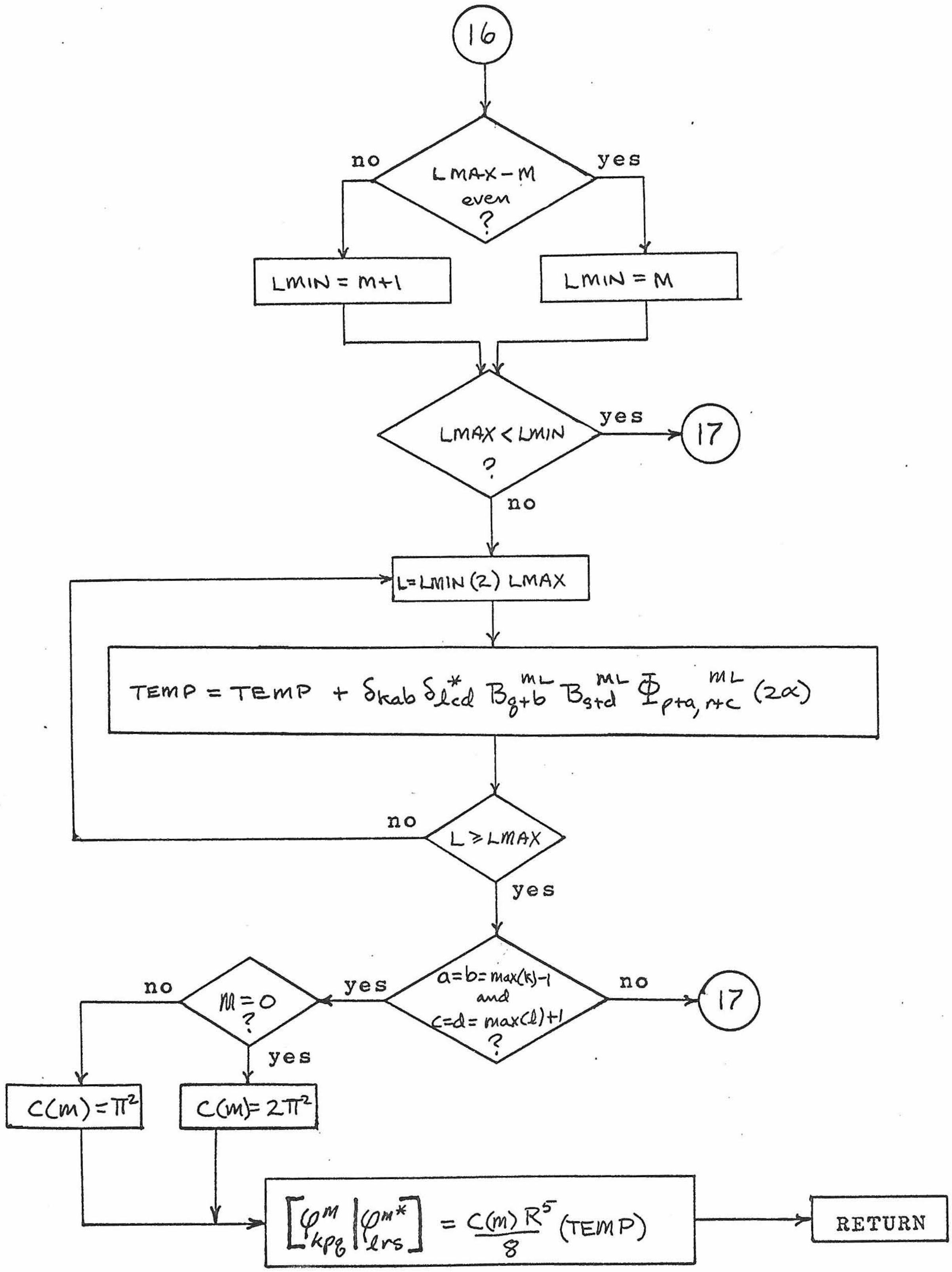



15
$a = 0(1)\max(\ell)+1$
$b = 0(1)\max(\ell)+1$
$TEMP\,2 = TEMP\,2 + \delta^*_{\ell ab}(s+b+1)^{-1}A_{r+a}(2\alpha)$
no
$a = b = \max(\ell)+1$
yes
$\langle \varphi_{kpq} | \varphi^*_{\ell rs} \rangle = \frac{\pi^2 R^6}{4}(TEMP\,1)(TEMP\,2)$
14

eq. 2.28

The functions $\left[\varphi^{m}_{kpq} \middle| \varphi^{m*}_{\ell rs}\right]$ (see eqs. 2.52 and 2.52*)





16
no
LMAX − M even ?
yes
LMIN = M+1
LMIN = M
LMAX < LMIN ?
yes
17
no
L=LMIN (2) LMAX
TEMP = TEMP + $\delta_{kab}\,\delta^{*}_{lcd}\,B^{mL}_{q+b}\,B^{mL}_{s+d}\,\Phi^{mL}_{p+a,\,r+c}(2\alpha)$
no
L ≥ LMAX
yes
no
m = 0 ?
yes
a=b= max(k)−1 and c=d= max(l)+1 ?
no
17
yes
C(m) = π^2
C(m) = $2\pi^2$
$\left[\varphi^{m}_{kpq}\middle|\varphi^{m*}_{lrs}\right] = \frac{C(m)\,R^5}{8}$ (TEMP)
RETURN

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