VARIATIONAL METHOD APPLIED TO KNIGHT SHIFT

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This thesis presents a study of the application of the variational principle to periodic lattices. A calculation of the conduction Knight Shift in the Alkali Metals is chosen as an example of the calculations possible with this method. The Knight Shift is discussed with reference to the contributions of both the core and conduction electrons. The approximation of neglect of the effect of the core electrons as found in previous calculations is discussed and and its validity questioned.

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CHAPTER I

INTRODUCTION

The variational method is a well known method for the calculation of the ground state energy of a physical system. The variational method states that the expectation value of the Hamiltonian between trial wavefunctions is greater than or equal to the true energy, and only equal when the trial wavefunction is the exact ground state wavefunction[1]. This may be expressed as

$$E_t = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_o$$

where Ψ is the trial wavefunction, H the Hamiltonian of the system, and E_o is the ground state energy.

By picking wavefunctions orthogonal to the ground state, it is possible to apply the above principle to the calculation of the wavefunctions of excited states[1]. The variational principle then states that the best approximation to the correct wavefunction is one that minimizes the expectation values of the Hamiltonian. The principle can be applied to calculation of wavefunctions by choosing trial wavefunctions which are linear combinations of a set of basis functions with arbitrary coefficients. The coefficients are then adjusted to minimize the expectation value of the Hamiltonian.

An important use of the variational principle has been to show that the self-consistent Hartree function is the best product wavefunction for the calculation of the ground state energy of a system of electrons[2]. A better approximation to the true wavefunction, because the proper antisymmetric nature of the wavefunction is accounted for, is the determinantal wavefunction[3]. The one electron wavefunctions in this method involve the spin as well as the space coordinates of the electron. These wavefunctions are referred to as spin-orbitals.

In more recent applications to systems of many electrons, the variational principle has been applied to a set of basis functions which are themselves Slater determinants[4,5]. This set of determinants is chosen to include the ground-state configuration with appropriately chosen excited-state configurations. The use of this method for determining the polarization of the core electrons in a metal by the conduction electrons is discussed in a later chapter.

In this thesis, a variational method originally developed by Kohn[6] is applied to periodic lattices. Because of the periodicity of the metal, the wavefunctions are subject to boundary conditions at the surface of the unit cell. By taking account of these boundary conditions, a variational principle appropriate to periodic lattices can be derived. The derivation of this variational method will be discussed in Chapter III.

To show the usefulness of this method, a calculation of the Knight Shift in the alkali metals was undertaken. The Knight Shift is the line shift of the nuclear magnetic resonance frequency in metals as compared to non-conductors. This shift in resonance frequency is primarily determined by the interaction of the polarized s conduction electrons with the nucleus. Secondary effects may arise from polarization of the s core electrons by the conduction electrons. The contact interaction with the polarized s core electrons also contribute to the Knight Shift. However, previous calculations of this line shift for lithium[7] and sodium[8] by the variational method and for sodium[9], potassium[10], rubidium[11], and cesium[12] by the expansion method of Silverman[13] have lent support to the supposition that the contact interaction of the nucleus and the s wave conduction electron is sufficient to explain the line shift in these metals. The present calculation has applied the variational method to improvement of the calculation of the line shift in the higher alkalis by including higher ℓ states than those considered by Callaway.

While the present calculation neglects core polarization, a survey is given in Chapter II which describes the methods necessary to calculate this effect. The methods discussed are the Unrestricted Hartree-Fock method and the process of configuration interaction.

CHAPTER II

THE KNIGHT SHIFT

The Knight Shift is named for W. D. Knight, who observed that the resonance of copper nuclei in metals occurs at higher frequencies than in the diamagnetic salt - cuprous chloride[14]. The present discussion is limited to cubic systems. Bloembergen and Rowland[15] have pointed out that the effect of non-cubic symmetry is to induce line broadening and asymmetric line shape.

Experimental results have been tabulated in a review article by Knight[16]. He has pointed out that the line shift has the following dependencies:

(1) The resonance frequency in a metal is higher than in a non-metal for a given external field (with the exception of intermetallic compounds[15]);

(2) The frequency shift is directly proportionate to the applied field;

(3) The frequency shift increases with atomic number;

(4) The frequency shift is almost temperature independent;

(5) The frequency shift is reduced in metals whose conduction electrons are not of s-wave character.

A consisten theory to explain the above facts has been given by Townes, Herring and Knight[17]. It is based on the contact interaction of the nucleus with the polarized conduction electrons at the Fermi surface. These conduction electrons have a high probability density at the position of the nucleus. The spatial dependance of the interaction between the s electron and the nucleus is given by a Dirac δ-function. The magnetic interaction between higher ℓ-states would have electron and nucleon moments with character; such an interaction averages to zero in the cubic system[18].

According to Townes et al.[17] the increase in the field H due to the polarized conduction electrons, for the case of cubic symmetry, is $8\pi/3$ times the mean density of spin moments at the nucleus. The spin moment density at the nucleus can be written as

$$X_p \; M \; H \; \langle \, |\Psi_F(o)|^2 \rangle_{AV}. \tag{II-1}$$

where H is the magnetic field strength, X_p is the spin contribution to the macroscopic susceptibility per unit mass, M is the mass of one atom and $\langle \, |\Psi_F(o)|^2 \rangle_{AV}$ is the average probability density at the nucleus of all the electronic states on the Fermi surface. Therefore, for the line shift,

$$\frac{\Delta H}{H} = \frac{8\pi}{3} \; X_p \; M \langle \, |\Psi_F(o)|^2 \rangle_{AV} \tag{II.2}$$

An equivalent form can be written in terms of the hyperfine atomic splitting

$$\frac{\Delta H}{H} = \frac{hc\Delta\nu \, I \, X_p \, M \, \langle|\Psi_F(0)|^2\rangle_{AV}}{\mu_I \mu_e \, (2I+1) \, |\Psi_a(0)|^2} \qquad (II.3)$$

by use of Fermi's expression for the hyperfine energy splitting of the s term by the nucleus[19]. In equation II.3 $hc\Delta\nu$ is the hyperfine splitting in energy units, μ_e the Bohr magneton, μ_I the nuclear magnetic moment, I the nuclear spin and $|\Psi_a(0)|^2$ the probability density of the electron at the nucleus of a free atom. Following Kohn[8], the following abbreviations will be used for the probability densities in the metal and the free atom[16]

$$P_F = \langle|\Psi_F(0)|^2\rangle_{AV}; \quad P_A = |\Psi_A(0)|^2; \qquad = P_F/P_A.$$

In the interest of completeness, a classical derivation of II.2 will be given in Appendix A, as found in Slichter[18].

Equation II.3 has the correct dependence to explain the experimental results. First, it shows a higher frequency for the metal than the diamagnetic reference. Second, it is directly proportional to the applied field. Third, it indicates that P_F increases as the atomic number increases, since there is a greater attractive nuclear charge. Fourth, it is independent of temperature since X_p and P_F are largely independent of temperature. Finally it indicates that the line shift is smaller in metals with conduction electrons with little s character because the P_F depends upon the s character of the conduction electrons.

As mentioned in the introduction, there is a second mechanism in cubic crystals which can give rise to a line shift. This mechanism is polarization of the core electrons by the polarized conduction electrons. This effect has been assumed to be small in all calculations of the Knight Shift for the alkali metals[7,8,9,10,11,12]. However, such an assumption would not be valid, in the case of transition metals, where core polarization has been shown to contribute substantially to the Knight Shift[5]. In the interest of completeness, a brief discussion follows, which describes two methods of calculating the contribution to the Knight Shift due to polarization of the core electrons.

The effect of the conduction electrons on the core states can be calculated in two different ways. First, a single determinantal wavefunction can be used, and the effect of core polarization calculated by use of the Unrestricted Hartree-Fock Method[20,21,22]. Second, a set of determinantal wavefunctions can be used, with coefficients selected by perturbation theory[5] or by a variational method[3]. The use of a set of determinantal wavefunctions is referred to as the process of configuration interaction[3].

The one electron wavefunctions calculated from the usual Hartree-Fock method are restricted in the sense that wavefunctions whose angular part can be connected by the raising and lowering operators for the total angular momentum have the same radial dependance. This restriction must be relaxed in the case of a polarized conduction electron of a single determinantal wavefunction is to suffice.

With a polarized conduction electron there is a difference in the potential seen by core electrons with spin up and with spin down. This difference arises in the exchange term of the Hartree-Fock equation. These equations, using the free electron approximation to the Slater[23] average exchange energy, are

$$H_1 U_i(x_1) + \left[\sum_{k=1}^{N} e^2 \int \frac{U_k^*(x_2) U_k(x_2)}{r_{12}} \, dx_2 - 3e^2 \left\{ \frac{3}{8\pi} \sum_{k=1}^{N} U_k^*(x_1) \, U_k(x_1) \right\}^{1/3} \right] U_i(x_1) = E_i U_i(x_1) \qquad \text{(II.4)}$$

where H_1 is the kinetic and potential energy for the electron at x_1, including the potential due to the contact interaction. The exchange term in the above equation II.4 will contribute only between electrons with parallel spins, because of the orthogonality of the spin wavefunctions. The effect of relaxing the restriction on the spin laddar operator is to change the exchange term to

$$- 3e^2 \left\{ \frac{3}{4\pi} \left(\frac{N_{\pm}(r)}{N(r)} \right) \sum_{k=1}^{N} U_k^*(x_1) \, U_k(x_1) \right\} U_i(x_1) \qquad \text{(II.5)}$$

where $N\pm/N$ is the fraction of electrons with ± spin at a radius r from the nucleus[21]. For equal numbers of electrons of spin up and spin down, the exchange term returns to its original form as found in equation II.4. With $M_s \neq 0$, however, the exchange term gives rise to a net polarization of the spins at the nucleus from the s wave core electrons. This may give a positive or negative contribution to the total Knight Shift depending on the relative splitting of each of the s wavefunctions at the origin[22].

Since a single determinantal wavefunction is used for this type of calculation, a parametric dependence on spin is used in place of solving the spin degeneracy problem. This means that (s)(s+1) is no longer a good quantum number. However, Korringa[24] has shown that important consequences follow from the fact that (s)(s+1) is a good quantum number in the physical problem. He has shown that there is an approximate relationship which holds between the Knight Shift and the relaxation time.

$$\tau \left(\frac{\Delta H}{H}\right)^2 = \frac{\hbar}{\pi k T g^2} \qquad \text{(II.6)}$$

where τ is the relaxation time, T is the temperature, g is the nuclear Lande factor and k is Boltzmann's constant.

The expression is approximate, in the sense that exchange and other correlations are neglected, so discrepancy between the theoretical and experimental values may be expected. Korringa's relaxation time is in fact, shorter than the observed times[18]. This observed discrepancy is due to the neglect of exchange correlations.

Of immediate interest to this discussion is the fact that the non-diagonal matrix elements of the contact Hamiltonian give rise to the relaxation time, while the diagonal elements account for the line shift. The main contribution to the relaxation time comes from processes in which the spin moment of momentum is conserved. Since (s)(s+1) is not a good quantum number, the Unrestricted Hartree-Fock is not a suitable starting point for the derivation of a Korringa type relationship for the core Knight Shift and relaxation time. However, the Unrestricted Hartree-Fock method does have the advantage of making a direct calculation of the polarization of the s wave core electrons using a single determinantal wavefunction.

A correct wavefunction, which is an eigenfunction of S^2, may be obtained by the addition of different excited configurations to the ground state configuration. The coefficients of these admixtures will be the same for both spins if there is no external polarization. However, when the conduction electron is polarized, the admixture of configuration with parallel spin orbital will be favored due to the exchange term in the Hartree-Fock equation. This favoring occurs because the exchange term lowers the interaction energy for parallel spins. By the addition of enough configurations, the correct wavefunction may be approximated as closely as desired. Once the correct wavefunction is known, the Knight Shift contribution due to core polarization may be calculated and the connection between the Knight Shift and relaxation time may be derived. This has been done by Yafet and Jaccarino[5,25]. They have shown that a Korringa type relationship holds for core polarization in the transition metals provided that only those configurations which keep the excited core electrons on the same atom are used.

Yafet and Jaccarino[5,25] have calculated the configuration interaction, using wavefunctions calculated from the Hartree-Fock equations, and applying the symmetry and equivalence restriction of Nesbet[4]. They further restricted themselves to configurations whose energy difference from the ground state was of the order of the exchange integral. In particular Yafet and Jaccarino[5] report that for a transition metal the Knight Shift is

$$\frac{\Delta H}{H} = \frac{4\pi}{3} (\gamma e\hbar)^2 \left(\langle \Psi_s^2 (0) \rangle - \left| \Psi_{cp}(0) \right|^2 \kappa \right) \eta \tag{II.7}$$

where the core polarization effect $\left| \Psi_{cp}(0) \right|^2$ is different in sign from the conduction term $\langle \Psi_s^2(0) \rangle$. κ is the degeneracy of the d state in the transition metal and η is the density of the states for one direction of the spin at the Fermi surface. They also reported that a Korringa type relationship does hold, and that the important contributions for the relaxation time come from the non-diagonal terms. However, the Korringa type relationship for the core polarization in the transition metals is reduced by a factor which depends upon the degeneracy of the d state. This relationship is

$$\left(\frac{1}{T}\right)_{cp} = \frac{4\pi}{\hbar} \left(\frac{\gamma_n}{\gamma_e}\right)^2 \left(\frac{\Delta H}{H}\right)^2 k_B T \left\{ \frac{1}{3} f^2 + \frac{1}{2} (1-f)^2 \right\} \tag{II.8}$$

where f is the fractional character of the Γ_5 d orbital at the Fermi surface.

The advantage of calculating the configuration interaction is the good quality of the wavefunction. It is a better approximation than the Unrestricted Hartree-Fock method. The results obtained by calculating configuration interaction are, therefore, more reliable.

CHAPTER III

THE VARIATIONAL METHOD

Variational methods have been employed to solve Schroedinger's Equation for various physical situations. Kohn[6] developed a system for applying this powerful method to periodic lattices.

Following Kohn[6] the present discussion investigates the one dimensional case and generalizes the result to three dimensions. The boundary value problem for the one dimensional lattice can be expressed as

$$\left(- \frac{d^2}{dx^2} + V(x) - E_k \right) \Psi_k = 0, \qquad \text{(III.1)}$$

$$\Psi_k(a) = e^{2ika} \Psi_k(-a), \qquad \text{(III.2a)}$$

$$\Psi_k'(a) = e^{2ika} \Psi_k'(-a), \qquad \text{(III.2b)}$$

where the Hamiltonian $H = - \frac{d^2}{dx^2} + V(x)$, E_k is the energy eigenvalue for the state Ψ_k, and k is the wave number, defined in the standard way, which characterizes the state Ψ_k.

Kohn's variational method is based on the study of functionals of the form

$$I = \int_{-a}^{+a} \Psi_k^* \left[H-E_k\right] \Psi_k \, dx \qquad (III.3)$$

These functionals have been used to calculate stationary values for the energy levels of the bound state as well as phase shifts for scattering problems[26,27].

The first variation of III.3 can be written as

$$\delta I = \int_{-a}^{+a} (\delta\Psi_k^*) \left[H-E_k\right] \Psi_k \, dx + \int_{-a}^{+a} \Psi_k^* \left[H-E_k\right] \delta\Psi_k \, dx$$

$$= \int_{-a}^{+a} \left(-\Psi_k^* \frac{d^2}{dx^2} \delta\Psi_k + (\delta\Psi_k) \frac{d^2}{dx^2} \Psi_k^*\right) dx, \qquad (III.4)$$

where the reduction has been accomplished using the fact that both Ψ_k and Ψ_k^* are eigenfunctions of H for the eigenvalue E_k. The integrand of III.4 can be written as the derivative of a function G, defined by

$$G = \Psi_k^{\prime *} \delta\Psi_k - \Psi_k^* \delta\Psi_k', \qquad (III.5)$$

where Ψ_k' is the x-derivative of Ψ_k. G' is then integrand of III.4 as can be checked by differentation of G. The integration can then readily be accomplished, yielding

$$\delta I = G(a) - G(-a). \qquad (III.6)$$

In order to construct a variational principle using δI, it is necessary to construct a quantity whose first variation is equal to δI, which, preferably, contains only Ψ_k and Ψ_k^* and their derivatives, evaluated at the boundaries. Such a quantity is

$$M_1 = -\Psi_k^{\prime *}(a) \; e^{ika} (\Psi_k(a) \; e^{-ika} - \Psi_k(-a) \; e^{ika}) + \qquad \text{(III.7)}$$
$$\Psi_k^{*}(a) \; e^{ika} (\Psi_k^{\prime}(a) \; e^{-ika} - \Psi_k^{\prime}(-a) \; e^{ika})$$

It can be shown that $-\delta M_1 = \delta I$ by using the boundary conditions III.2a and III.2b. A variational principle can, therefore, be constructed, since the first variation of the quantity $I + M_1$ is zero. However, for purposes of symmetry, it is convenient to construct a second quantity M_2, defined by

$$M_2 = -\Psi_k^{\prime *}(-a) \; e^{-ika} (\Psi_k(a) \; e^{-ika} - \Psi_k(-a) \; e^{ika})$$
$$+ \Psi_k^{*}(-a) \; e^{-ika} (\Psi_k^{\prime}(a) \; e^{-ika} - \Psi_k^{\prime}(-a) \; e^{ika}).$$

(III.8)

It can be shown that $-\delta M_2 = \delta I$ in the same manner as before. If

$$M = \tfrac{1}{2} (M_1 + M_2), \qquad \text{(III.9)}$$

then it is possible to write a variational principle for the quantity K, defined as

$$K = I + M. \qquad \text{(III.10)}$$

K is stationary by construction.

The quantity K is also real, as can be seen from the following arguments. First, the imaginary part of I is given by

$$\operatorname{Im}\left\{ I \right\} = \frac{1}{2}\left[\Psi_k \Psi_k^{*\prime} - \Psi_k^{*} \Psi_k^{\prime} \right]_{-a}^{+a} \qquad \text{(III.11)}$$

Second, the imaginary part of M is given by

$$\operatorname{Im}\left\{ M \right\} = -\Psi_k^{*\prime}(a) \quad \Psi_k(a) + \Psi_k^{*}(a)\,\Psi_k^{\prime}(a) + \Psi_k^{*\prime}(-a)\,\Psi_k(-a)$$

$$- \Psi_k^{*}(-a)\,\Psi_k(-a) = -\tfrac{1}{2}\left[\Psi_k \Psi_k^{*\prime} - \Psi_k^{*} \Psi_k^{\prime} \right]_{-a}^{+a}$$

$$\text{(III.12)}$$

Comparison of III.11 and III.12 establishes the reality of K. A simplified form of the variational principle can, therefore, be written, namely:

$$K = \operatorname{Re}\left[\int_{-a}^{+a} \Psi_k^{*} \left[H - E_k \right] \Psi_k \, dx + \left(\Psi_k(-a)\,\Psi_k^{*\prime}(a)\, e^{2ika} \right.\right.$$

$$\left.\left. - \Psi_k(a) \quad e^{-2ika} \right) \right] = \text{stationary} \qquad \text{(III.13)}$$

The equivalent functional to III.3 for the three dimensional lattice is

$$I = \int_{\Omega} \Psi_k^{*} \left[H - E_k \right] \Psi_k \, d\omega \qquad \text{(III.14)}$$

where indicates the enclosed volume of the polyhedral unit cell. The boundary value problem for the three dimensional lattice can be expressed as

$$(-\nabla^2 + V(r) - E_k)\,\Psi_k = 0 \qquad \text{(III.15)}$$

$$\Psi_k(r') = \exp\,(i\,\underset{\sim}{k}.\underline{\tau})\,\Psi_k(r) \qquad \text{(III.16a)}$$

for all r and r' on the surface of polyhedron

$$\frac{\partial\Psi_k(r')}{\partial\,\eta} = -\exp\,(i\,\underset{\sim}{k}.\underline{\tau}_r)\,\frac{\partial\Psi_k(r)}{\partial\,\eta} \qquad \text{(III.16b)}$$

for all r and r' on the surface of polyhedron.

In all the above expressions $\partial/\partial\eta$ is the differentiation along the outward normal, and $\underline{\tau}_r$ is the translation vector $\underset{\sim}{r}' - \underset{\sim}{r}$. The negative sign is therefore due to the fact that the outward normals of $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ are in opposite directions. The first variation in the functional III.14 can be written as

$$\delta I = \int_\Omega (\delta\Psi_k^* \left[-\nabla^2 + V(r) - E_k\right]\Psi_k + \Psi_k^*\left[-\nabla^2 + V(r) - E_k\right] \delta\Psi_k)\,d\omega = (\delta\Psi_k \frac{\partial^2\Psi_k^*}{\partial\eta^2} - \Psi_k^* \frac{\partial^2\delta\Psi}{\partial\eta^2})\,d \qquad \text{(III.17)}$$

where Schroedinger's equation has been used to simplify the result. δI can, in analogy with the one dimensional case, be rewritten as the surface integral

$$\delta I = \int_S (\delta\Psi_k \frac{\partial\Psi_k^*}{\partial\eta} - \Psi_k^* \frac{\partial\delta\Psi_k}{\partial\eta})\,dS. \qquad \text{(III.18)}$$

Now it is possible to repeat the arguments of the one dimensional case, writing the right side of III.18 as the first variation of a functional Q. From consideration of the one dimensional case it is plausible that an equivalent variational principle can be derived for the three dimensional case by considering only the real part of III.18. Therefore, the quantity of interest will be

$$\mathrm{Re} \int_S \delta\Psi_k(r) \frac{\partial \Psi_k^*(r)}{\partial \eta} \, ds$$

$$= \mathrm{Re} \int_S \frac{\partial \Psi_k(r)}{\partial \eta} \delta\Psi_k^*(r) \, ds$$

$$= \mathrm{Re} \int_S \frac{\partial \Psi(r')}{\partial \eta} \delta\Psi^*(r') \, ds,$$

which by III.16a is

$$\mathrm{Re} \int_S - \frac{\partial \Psi_k(r)}{\partial \eta}\Psi \; \delta\Psi^*(r') \exp(i \, \underline{k} \cdot \underline{\tau}_r) \, ds.$$

(III.19a)

Similiarly the second part of III.18 can be shown to be

$$\mathrm{Re} \int_S - \Psi_k^*(r) \frac{\partial \delta\Psi_k(r)}{\partial \eta} \, ds$$

$$= \mathrm{Re} \int_S - \frac{\partial \delta\Psi_k(r)}{\partial \eta} \Psi^*(r') \exp(i\underline{k} \cdot \underline{\tau}_r) \, ds.$$

(III.19b)

Combing these last two results give

$$\delta\ (\mathrm{Re}\,I) = -\delta \left(\mathrm{Re} \int_S \frac{\partial \Psi_k(r)}{\partial \eta}\, \Psi_k^*(r')\, \exp\,(i\, \underset{\sim}{k} \cdot \underset{\sim}{\tau}_r)\, ds \right),$$

which allows the variational principle for the three dimensional lattice to be written as

$$J = \mathrm{Re}\left[\int_{\Omega} \Psi_k^* \left[-\nabla^2 + V(r) - E_k \right] \Psi_k\, d\omega + \int_S \frac{\partial \Psi_k(r)}{\partial \eta}\, \Psi_k^*(r')\, \exp\,(i\underset{\sim}{k} \cdot \underset{\sim}{\tau}_r)\, ds \right]$$

$$= \text{stationary.} \qquad \text{(III.20)}$$

CHAPTER IV

APPLICATION OF THE VARIATIONAL METHOD TO THE KNIGHT SHIFT

The application of the variational principle derived in the preceding chapter (Equation III.20) to the calculation of P_F for the contact Knight Shift was first made by Kohn[7,8]. Following the arguments of Kohn[7], the unit cell is approximated by the equivalent Wigner-Seitz sphere of radius r_s. The boundary value problem may be written, as in the preceding chapter, as

$$(-\nabla^2 + V(r) - E_k)\,\Psi_k(r) = 0,\ r<r_s, \qquad \text{(IV.1)}$$

$$\Psi_k(r) = e^{2ikr_s \cos\theta}\,\Psi(-r),\quad r=r_s, \qquad \text{(IV.2a)}$$

$$\frac{\partial\Psi(r)}{\partial r} = -\,e^{2ikr_s \cos\theta}\,\frac{\partial\Psi(-r)}{\partial r},\quad r = r_s \qquad \text{(IV.2b)}$$

The wavefunction inside the sphere can be expressed as the expansion

$$\Psi_k(a) = C_o\,R_o(r)\,P_o(\cos\theta) + i\,C_1\,R_1(r)\,P_1(\cos\theta) + C_2\,R_2(r)\,P_2\,(\cos\theta) + \ldots, \qquad \text{(IV.3)}$$

where R_ℓ is a radial function which satisfies Schroedinger's equation and P_ℓ the ℓth Legendre polynomial. The R_ℓ are normalized such that for all ℓ, $R_\ell(r_s) = 1$.

Since the above solution IV.3 satisfies Schroedinger's equation, the variational equation III.20 reduces to

$$J \doteq \int_S \frac{\partial \Psi_k(r)}{\partial r} \Psi^*(-r) e^{-2ikr_s \cos\theta} \sin\theta \, d\theta$$

$$= \text{stationary} \qquad \text{(IV.4)}$$

When IV.3 is substituted into IV.4, the stationary condition allows determination of the C_ℓs. Equation IV.4 becomes

$$J = \sum_{\ell, j} \int_S i_\ell i_j C_\ell C_j R_\ell(r) \frac{\partial R_j(r)}{\partial r} P_\ell(\cos\theta)$$

$$P_j(\cos\theta) \, e^{2ikr_s \cos\theta} \sin\theta \, d\theta$$

$$= \text{stationary}, \qquad \text{(IV.5)}$$

where i_ℓ is defined by

$$i_\ell = \begin{cases} i & \ell \text{ odd} \\ 1 & \ell \text{ even} \end{cases}$$

Therefore

$$\frac{\partial J}{\partial C_j} = 0 = \sum_\ell \int i_\ell i_j C_\ell R_\ell(r) \frac{\partial R_j(r)}{\partial r} P_\ell(\cos\theta)$$

$$P_j(\cos\theta) \, e^{2ikr_s \cos\theta} \sin\theta \, d\theta. \qquad \text{(IV.6)}$$

This is a set of homogeneous equations for the coefficient C_ℓ. The equations have a solution if

$$\begin{vmatrix} 2L_0I_{00} & (L_0 + L_1)\, iI_{01} & (L_0 + L_2)\, I_{02} \cdots \\ (L_0 + L_1)\, iI_{01} & -2L_1I_{11} & (L_1 + L_2)\, i\, I_{12} \cdots \\ (L_0 + L_2)\, I_{20} & (L_1 + L_2)\, iI_{21} & 2L_2I_{22} \quad \cdots \\ \vdots & \vdots & \vdots \end{vmatrix} = 0 \qquad (IV.7)$$

where the normalization condition $R_\ell(r_s) = 1$ is used in simplifying the R dependance of IV.7. Thus

$$L_\ell = \left[\frac{\partial R_\ell(r)}{\partial r} / R_\ell(r) \right]_{r=r_s} \qquad (IV.8a)$$

and

$$I_{ij} = \int_{-1}^{+1} e^{-2ikr_s \cos\theta} P_i(\cos\theta)\, P_j(\cos\theta)\, d(\cos\theta) \qquad (IV.8b)$$

It is observed that I_{ij} is imaginary or real depending on whether P_i (cos θ) x P_j (cos θ) is an odd or even function. It follows that the determinant is always reals

With the coefficients C_ℓ known, the quantity P_F can be calculated from

$$P_F = \left|\Psi_F(o)\right|^2 / \int \Psi^* \Psi \, d \; . \qquad \text{(IV.9)}$$

Since $R_\ell(o) = 0$ if ℓ greater than 0

$$\left|\Psi(o)\right|^2 = C_o^2 \, R_o(o)^2. \qquad \text{(IV.10)}$$

Because of the orthogonality of the Legendre polynomial,

$$\int \Psi^* \Psi d = \sum_\ell \frac{4\pi}{2\ell+1} C_\ell^2 \int_0^{r_s} R_\ell^2(r) \, r^2 \, dr. \qquad \text{(IV.11)}$$

Therefore,

$$P_F = C_o^2 \, R_o^2(o) / (\sum_\ell \frac{4\pi}{2\ell+1} C_\ell^2 \int_0^{r_s} R_\ell^2(r) \, r^2 \, dr.) \qquad \text{(IV.12)}$$

The calculation of the normalized wavefunction is easily seen from IV.11. The normalized C_ℓ is related to the C_ℓ given by the homogeneous equation as

$$C_{\ell \text{ normalized}} = C_{\ell \text{ homogeneous}} / \left[\Psi^* \Psi \, d\tau\right]^{1/2} \qquad \text{(IV.13)}$$

It is now possible to check the satisfaction of the boundary condition IV.2a.

From this condition it follows that

$$(C_o\, P_o(\cos\theta) + C_2\, P_2\,(\cos\theta)\; .\;.\;.) + i\,(C_1P_1(\cos\theta) + C_3\,P_3\,(\cos\theta) + .\;.\;.)$$

$$= (C_oP_o(\cos\theta) + C_2\,P_2(\cos\theta) + .\;.\;.\;) - i(C_1P_1(\cos\theta) + C_3P_3\,(\cos\theta)\;.\;.\;.)\quad e^{2ikr_s\cos\theta},$$

(IV.14)

which can be put in the convenient form

$$\frac{(C_1P_1(\cos\theta) + C_3P_3(\cos\theta) + .\;.\;.)}{(C_oP_o(\cos\theta) + C_2P_2\,(\cos\theta) + .\;.\;.)} \Big/ \tan\,(k\, r_s\,\cos\theta) = 1.$$

(IV.15)

Equation IV.15 provides a check on the wavefunction for all values of θ. It is to be noted that satisfaction of the boundary conditions requires the mixing of even and odd parity states. Such a mixing requires the addition of higher angular momentum states even though their percentage of the total wavefunction on the boundary is very small. This has been calculated by renormalizing the wavefunction such that

$$\Psi = \sum_{\ell} a_\ell\, \phi_\ell, \qquad \text{(IV.16)}$$

where ϕ_ℓ is the wavefunction corresponding to the angular momentum states ℓ, normalized to unity such that

$$\sum_{\ell} a_\ell^{\;2} = 1.$$

on the Wigner-Seitz sphere. These wavefunctions are reported in Appendix B.

CHAPTER V

DISCUSSION AND RESULTS

The results of the calculation of the metalic wavefunction for the alkali metals are reported in Appendix B and the programs developed for this calculation are given in Appendix C. The potentials used are those found in the literature. The Seitz[7] and Prokofjew[8,9] potentials have been included since the wavefunctions, calculated by the variational method, for these potentials, have not previously been reported. Callaway and coworkers have tabulated potentials for potassium[28], rubidium[11] and cesium[12]. The Rb and Cs potentials are adaptations of the potentials of Hartree and Hartree[29] for the rubidium ion and Sternheimer's 6S cesium potential[30]. The potasium potential is constructed so that the exchange potential for a given L is found from an approximate wavefunction for a valance electron state of that L. The present calculation has used an electron potential which has the exchange potential calculated from approximate S wavefunctions.

The solution of Schroedinger's equation was simplified by the choice of atomic units as defined by Slater[31]. The numerical integration of the radial equation was done by the method of Runge-Kutta-Nystrom[32] on the 7040 computer installation at McMaster University.

The starting equations for the outward integration are given by Hartree[33].

Extra solutions of the variational equation were found which did not obey the proper boundary condition. The form of equation IV.4 is such that there are two possible types of solutions. If $\Psi(r)$ is normalized to one at the boundary, $\frac{\partial\Psi(r)}{\partial r}$ must go to zero at the boundary. This satisfies the proper boundary conditions as given by IV.2a and IV.2b.

However, the variational equation will be satisfied if $\frac{\partial\Psi(r)}{\partial r}$ equals one and $\Psi(r)$ equals zero at the boundary. This situation will never satisfy the proper boundary conditions. It will, in fact, satisfy boundary conditions in which the roles of the derivative and wavefunction are exchanged.

Herman and Skillman[34] have calculated approximate potentials for all of the alkali ions using the Hartree-Fock-Slater equations. They have calculated the free atom potential and have written the ionic potential in the form

$$V(r) \begin{cases} \text{atomic potential} & r < r_o \\ -2Z/r & r > r_o \end{cases} , \qquad (V.1)$$

where r_o satisfies the equation $r_o V(r_o) = -2Z$. The wavefunctions for these potentials are not reported, but the P_F values are given to show the effect that different potentials have on the Knight Shift. The and P_F values are compared to those reported by Callaway and coworkers[9,10,11,12] and the experimental results reported by Knight[16] in Table 1.

Present calculation is for angular momentum states up to $\ell = 9$. Kohn has gone to $\ell = 6$.[7,8]

TABLE 1

			KOHN	PRESENT	CALLAWAY	EXPERIMENT
		P_A*10^3	P_F*10^3	P_F*10^3	P_F*10^3	
Li	Herman & Skillman			.107 .480		
	Seitz	.223[7]	.110 .49	.108 .484		.43*
Na	Herman & Skillman			.569 .831		
	Prokofjew	.685[89]	.555 .81	.557 .813	.566 .826	.72*
K	Herman & Skillman			.766 1.030		
	Callaway	.743[10]		.576 .775	.862 1.16	
Rb	Herman & Skillman			1.572 .800		
	Callaway	1.965[11]		1.414 .720	2.162 1.10	1.00**
Cs	Herman & Skillman			1.966 .76		
	Callaway	2.6[12]		2.012 .77	3.0 1.2 2.89+ 1.11+	1.3**

* X_p from direct spin resonance experiments.

** X_p from theoretical calculation of Pines.

\+ Revised calculation by Callaway[12a].

It is observed that P_F increases as expected for the higher atomic numbers. There is a substantial discrepency between the two theoretical estimates of P_F for Rb, K, and Cs. Callaway's results agree more closely with the experimental values. The variational method predicts a lower value than that predicted by Callaway. It is, therefore, useful to review the approximations made in the present work.

The spherical approximation has been used for all of the alkali metals. However, comparison of the ionic radii and the lattice constant, as shown in Table 2, indicates that this approximation should have roughly equal validity for all of the alkali metals.

TABLE 2

	Lattice Constant in Angstrom's[35]	Ionic Radii in Anstrom's[36]	Ratio
Li	3.50	.78	.624
Na	4.28	.98	.457
K	5.33	1.33	.499
Rb	5.62	1.49	.530
Cs	6.05	1.65	.545

The agreement with experiment achieved in the case of lithium[7] and sodium[8] suggests that this approximation is valid for these cases and therefore should be valid for all of the alkalis.

The only approximation which may be in doubt is the neglect of core polarization in the higher alkali metals. This effect is negligible in the case of sodium and lithium, as shown by the argument with experiment of the calculations of Kohn[7] and Kohn and Kjeldaas[8], but its size in the case of the higher alkalis has not been investigated.

The calculations of Callaway[10,11,12] may be thought to be a partial verification of the neglect of core polarization, since he has also used the spherical approximation. Callaway's wavefunction is expanded in powers of k according to the method of Silverman[13]. The wavefunction Ψ is written

$$\Psi_k = e^{ik.r} U_k,$$

where U_k is expanded by Silverman[13] as

$$U_k = U_o + U_1 k + U_2 k^2.$$

Callaway[9,10,11,12,28] has rewritten the results of Silverman as

$$U_k = U_o + ik \cos \theta \, U_1 + k^2 (U_2 P_2(\cos \theta) + \phi_o),$$

where ϕ_o is the s part of the U_2 as given by Silverman[13] minus a constant term which has been neglected. The s part of U_2 has been given by Silverman as

$$\frac{1}{3} r f_p - \frac{1}{6} r^2 U_o + E_2 (\partial U_o / \partial E)_{E=E_o} + C_s U_o,$$

while Callaway quotes the same as

$$\phi_o = \frac{1}{3} r U_1 + \frac{1}{6} r^2 U_o + E_2 (\partial U_o / \partial E)_{E=E_o},$$

where $f_p = U_1 + rU_o$ and $U_1(r_s) = 0$ from the boundary conditions.

The significance of this constant term C_sU_o has been given by Brooks[37]. This term is necessary in order to normalize the wavefunction independent of k.

A second point to be considered in Callaway's calculations is the effect of higher order terms. Callaway has expanded the periodic part of the Bloch wavefunction to second order in k. A expansion of the Bloch wavefunction in powers of k has been developed by R. Taylor[38] (Private communication) to account for the effect of the high order terms. His results for rubidium ($P_F = 1.451$) are similar to those of the present variational calculation ($P_F = 1.414$). This seems to indicate that the effect of the higher order terms is to lower the P_F value are that Callaway's calculations do not necessarily vindicate the approximation of neglecting core polarization. Calculations of core polarization in transition metals[5,25] indicate that the effect reduces the P_F value. Consideration of the exchange term in the Hartree-Fock equation indicates that a polarized conduction electron will repel a core electron of parallel spin less than it will on electron of antiparallel spin. This suggests that the polarized d conduction electrons in the transition metal causes a splitting of the s core electrons which favors a reduction in P_F[5,25]. The direction of the effect of polarized s conduction electrons is, however, not clear.

Therefore the calculation of the Knight Shift for the higher alkali metals should entail a numerical estimate of the core polarization. It seems from the present work that the contact term is insufficient to cause the total Knight Shift.

APPENDIX A

Slichter has given the following classical derivation of equation II.2 in his book "Principles of Magnetic Resonance".[18] Slichter represents the spining nucleus as a charge q going around a circular path of radius a with speed v. This is effectively a current loop of current q/CT where T is the period of motion.

It is necessary to find the magnetic field due to the nucleus in the direction perpendicular to the current loop (q direction), averaged over the electron probability density. Symmetry indicates that only the z component is important. This component is

$$\bar{H}_z = \int_\tau H_z(r) \; |U(r)|^2 \; d\tau \qquad \text{A.1}$$

A sphere of radius a, centered at the center of the nucleus, divides space into two regions, in each of which H can be found as the negative gradient of a scalar magnetic potential.

The integration of A.1 over angles leads to a constant field H_o inside the sphere and a dipole field outside the sphere. The dipole field outside the sphere cannot contribute to the average indicated in equation A.1. Therefore

$$\bar{H}_z = \int_0^a H_c \, |U_c(o)|^2 \, d\tau = H_c \, U(o)^2 \, \frac{4\pi}{3} a^3 \qquad \text{A.2}$$

where, in performing the integration, the approximation has been made that U(r) varies little over the nucleus. The constant field H_c can be evaluated at the center. $\underline{H}_c$ is given by

$$\underline{H}_c = \frac{q}{c} \frac{\underline{r} \times \underline{v}}{r^3} = \frac{q}{c} \frac{v}{a^2} \underline{k} \qquad A.3$$

where $\underline{k}$ is the unit vector in the z direction. The magnetic moment of the nucleus has magnitude $i\pi a^2$, where i is the current. In terms of the nuclear charge, then,

$$\mu_n = \frac{q}{c} \frac{1}{\;} \pi a^2 \underline{k} = \underline{k} \frac{qav}{2c} \qquad A.4$$

This gives the connection between the field at the center of the sphere and the magnetic moment of the nucleus as

$$\underline{H}_c = \frac{2\underline{\mu}_n}{a^3} \qquad A.5$$

and

$$\underline{k} H_z = \frac{8\pi}{3} \underline{\mu}_n U^2(o) \qquad A.6$$

By use of equation A.6, the energy of interaction with the electron moment can be written

$$E = -\underline{\mu}.\underline{H} = -\frac{8\pi}{3} \underline{\mu}_e \cdot \underline{\mu}_n U^2(o) \qquad A.7$$

The Hamiltonian H which will give the above energy can be written, with the aid of the Dirac delta function, in terms of the nuclear and electron spins $\underline{I}$ and $\underline{S}$. Using the gyromagnetic ratios γ_e and γ_n, defined by

$$\underline{\mu}_e = -\gamma_e h \underline{S} \quad \text{and} \quad \underline{\mu}_n = \gamma_n h \underline{I} \qquad A.8$$

the Hamiltonian can be written as

$$H = \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \underline{I}.\underline{S} \; \delta(r) \qquad \text{A.9}$$

This is the contact Hamiltonian which has been used to find the line shift. If $\underline{r}_\ell$ is the radius vector to the ℓth electron and $\underline{R}_j$ is the vector to the jth nucleus, the Hamiltonian for all electrons in the presence of all nuclei can be written as

$$H_{en} = \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \sum_{j,\ell} \underline{I}_j.\underline{S}_\ell \; \delta(\underline{r}_\ell - \underline{R}_j) \qquad \text{A.10}$$

The weakness of the contact interaction enables it to be treated by perturbation theory with respect to the states of the electrons and the nuclear spin. For low energy processes that do not excite the plasma[39] modes, the electron may be considered weakly interacting. The wave function for the nuclei and the electrons can be written in the form

$$\Psi = \Psi_e \Psi_n \qquad \text{A.11}$$

The transitions of interest on the transitions of the nuclear system from Ψ_n to Ψ_n'. These transitions of the nuclear system leave the electron state unchanged. Therefore, an effective Hamiltonian for the nuclei, H', can be defined by

$$H' = \int \Psi_e^* \, H \, \Psi_e \, d\tau_e \qquad \text{A.12}$$

where the prime signifies that the nuclear part of the Hamiltonian still contains operators and $d\tau_e$ indicates integration over the electron (spacial and spin) coordinates

Ψ_e is written

$$\Psi_e = \frac{1}{\sqrt{N}} \sum_P (-1)^P P\, \Psi_{k_1 s_1}(1)\, \Psi_{k_2 s_2}(2) \ldots \Psi_{k_N s_N}(N), \qquad A.13$$

where k_i and s_i are the space-state and spin quantum numbers of the ith electron. The operator P is the permutation operator, so that Pauli's exclusion principle will hold. The one electron states are Bloch functions with appropriate spin eigenfunctions

$$\Psi_{ks} = U_{\underset{\sim}{k}}(r)\, e^{i\underset{\sim}{k}.\underset{\sim}{r}}\, \phi_s, \qquad A.14$$

where $U_k(r)$ is a periodic function and ϕ_s is a spin function.

The effective Hamiltonian seen by the jth nuclear spin,

$$H'_j = 8\pi\, \gamma_e \gamma_n \hbar^2 \underset{\sim}{I}_j \cdot \int \Psi_e^* \sum_{\ell} \underset{\sim}{S}_{\ell}\, \delta(\underset{\sim}{r}_{\ell})\, \Psi_e\, d\tau_e$$

$$= \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \underset{\sim}{I}_j \cdot \sum_{\ell} \int \Big[\Psi_{k_1 s_1}(1)\, \Psi_{k_2 s_2}(2) \ldots\Big]$$

$$\underset{\sim}{S}_{\ell}\, \delta(\underset{\sim}{r}_{\ell}) \times \Big[\Psi_{k_1 s_1}(1)\, \Psi_{k_2 s_2}(2) \ldots\Big] d\tau_1\, d\tau_2, \qquad A.15$$

where the center of coordinates has been taken at the jth nuclear site.

Here the simplification is possible since $\underset{\sim}{S}_{\ell}\, \delta(\underset{\sim}{r}_{\ell})$ involves only one electron and there are no contributing exchange terms.

The electrons are quantized along the z-direction by the external field H_o. Thus, the only contribution to A.15 comes from $S_{z\ell}$. A. 15 can be rewritten

$$\frac{8\pi}{3}\gamma_e\gamma_n h^2 I_{zj}\sum_{k,s}\left|U_k(o)\right|^2 m_s P(k,s) \qquad \text{A.16}$$

where P(k,s) is an occupation factor which has the value one if the state is occupied and zero if the state is not occupied. m_s is the eigenvalue of s_z for the state Ψ_{ks}. If the occupation function that is appropriate to thermalized electrons, A.16 can be rewritten

$$\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2 I_{zj}\sum_{k,s}\left|U_k(o)\right|^2 m_s\ f(k,s), \qquad \text{A.17}$$

where f(k,s) is the Fermi function

$$f(k,s) = f_{k,s}(E) = \frac{1}{1+\exp\left(E-E_F/_{kT}\right)} \qquad \text{A.18}$$

A single term of the sum in A.17 is

$$\frac{8\pi}{3}\gamma_n h I_{zj}\left[\gamma_e\hbar(½)\ f(k,½) + \gamma_e\hbar(-½)\ f(k,-½)\right]\left|U_k(o)\right|^2 \qquad \text{A.19}$$

where, apart from the negative sign since $\underline{\mu}_e = -\gamma_e\hbar\underline{S}$, the term in the bracket is the average contribution of state K to the z component of the electron magnetization of the sample. This can be denoted by μ_{zk}. The total of magnetization of the electrons is

$$\mu_z = \sum_k \mu_{zk} \qquad \text{A.20}$$

A total spin susceptibility, X_e^s, can be defined

$$\bar{\mu}_z = X_e^s H_o \qquad \text{A.21}$$

where, in analogy with A.20,

$$X_e^s = \sum_k X_k^s \qquad \text{A.22}$$

where X_k^s is the spin susceptibility at the electron in state k. Using A.17 for the total effective interaction for spin j gives

$$- \frac{8\pi}{3} \gamma_n I_{zj} \left[\sum_k \left| U_k(o) \right|^2 X_k^s \right] H_o \qquad \text{A.23}$$

The summation over k can be done by defining a density operator $g(E_k, A)$ such that the total number of states dN between energy surfaces E_k and $E_k + dE_k$ of area dA is

$$dN = dE_k \int_{Ek=constant} g(E_k, A)\, dA \qquad \text{A.24a}$$

$$= \rho(E_k)\; dE_k \qquad \text{A.24b}$$

Equations A.24a and A.24b are sufficient to define the density functions $g(E_k, A)$ and $\rho(E_k)$.

The summation in A.23 is now written

$$\int \left| U_k(o) \right|^2 X_k^s\; g(E_k, A)\; dE_k\; dA$$

It is reasonable to make the assumption that X_k^s depends only on the energy E_k ($X^s(E_k) = X^s(E_k)$) is zero for energies outside a small energy region of width kT around the Fermi Energy. For small values of energy the two spin states are fully populated and for large values neither state is populated. $\left|U_k(o)\right|^2$ varies slowly over this region of interest so that this quantity can be taken outside the integral in A.26. The result is

$$\sum_k \left|U_k(o)\right|^2 X_k^s = \langle |U_k(o)|^2 \rangle_{E_F} X_e^s \qquad \text{A.27}$$

where A24a and A.24b have been used to perform the summation. Finally the interaction with the jth nuclear spin is

$$- \gamma_n \hbar I_{zj} \left[\frac{8\pi}{3} \langle |U_k(o)|^2 \rangle_{E_F} X_e^s H_o \right] \qquad \text{A.28}$$

The term inside the bracket is equivalent to an extra magnetic field, H which reinforces the applied field H_o.

Therefore,

$$\frac{\Delta H}{H_o} = \frac{8\pi}{3} \langle |U_k(o)|^2 \rangle_{E_F} X_e^s \qquad \text{A.29}$$

is the equation of the Knight Shift and is identical with II.2 as $X_p^M = X_e^s$.

APPENDIX B

```
                          LITHIUM
PERCENTAGE OF WAVEFUNCTION AT BOUNDARY L = 0 TO 4
.2083  .7263  .0643  .0004  .0003
NORMALIZED COEFFICIENTS  L = 0 TO 4
 .006645 -.002773 -.000939  .000177  .000093
             WAVEFUNCTION R(L) AT POSITION X
 X =  L=     0          1          2          3          4
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.0100 -0.096455  0.000253  0.000000  0.000000  0.000000
0.0200 -0.187258  0.000996  0.000002  0.000000  0.000000
0.0300 -0.272705  0.002208  0.000008  0.000000  0.000000
0.0400 -0.353048  0.003870  0.000019  0.000000  0.000000
0.0500 -0.428508  0.005962  0.000037  0.000000  0.000000
0.0600 -0.499274  0.008466  0.000063  0.000001  0.000000
0.0700 -0.565527  0.011363  0.000099  0.000002  0.000000
0.0800 -0.627441  0.014638  0.000146  0.000003  0.000000
0.0900 -0.685184  0.018272  0.000207  0.000004  0.000000
0.1000 -0.738921  0.022251  0.000281  0.000006  0.000000
0.2000 -1.087932  0.077917  0.002063  0.000094  0.000005
0.3000 -1.179378  0.154699  0.006433  0.000449  0.000036
0.4000 -1.106144  0.244843  0.014195  0.001346  0.000144
0.5000 -0.932427  0.343924  0.026010  0.003140  0.000425
0.6000 -0.699788  0.449299  0.042451  0.006251  0.001024
0.7000 -0.434287  0.559044  0.064013  0.011164  0.002152
0.8000 -0.152862  0.671725  0.091130  0.018417  0.004087
0.9000  0.133228  0.786288  0.124192  0.028604  0.007191
1.0000  0.416455  0.902158  0.163589  0.042373  0.011913
1.2000  0.955707  1.135064  0.262600  0.083441  0.028482
1.4000  1.441683  1.366565  0.390410  0.147629  0.059410
1.6000  1.865188  1.594164  0.548936  0.241563  0.112160
1.8000  2.224289  1.816333  0.739869  0.372456  0.196258
2.0000  2.520810  2.032159  0.964731  0.548068  0.323483
2.2000  2.758529  2.241194  1.224939  0.776690  0.508069
2.4000  2.942175  2.443340  1.521866  1.067153  0.766909
2.6000  3.077408  2.639235  1.857178  1.429056  1.119931
2.8000  3.170467  2.830232  2.233014  1.872923  1.590433
3.0000  3.227415  3.017913  2.651824  2.410233  2.205472
3.0250  3.232285  3.041225  2.707333  2.484586  2.294040
3.0500  3.236683  3.064512  2.763558  2.560602  2.385370
3.0750  3.240632  3.087783  2.820513  2.638336  2.479605
3.1000  3.244133  3.111038  2.878198  2.717791  2.576751
3.1250  3.247203  3.134283  2.936623  2.799011  2.676923
3.1500  3.249848  3.157519  2.995791  2.882011  2.780161
3.1750  3.252080  3.180752  3.055711  2.966824  2.886551
3.2000  3.253908  3.203985  3.116388  3.053478  2.996167
3.2250  3.255309  3.226137  3.174898  3.137701  3.103504
3.2500  3.256263  3.246160  3.228396  3.215354  3.203251
3.2566  3.256442  3.251191  3.241957  3.235155  3.228828
```

```
NORMALIZED COEFFICIENTS  L = 5 TO 9
-.033113 -.122321  .066421  .007535  .008855
              WAVEFUNCTION R(L) AT POSITION X
 X =  L=     5           6           7           8           9
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.1250  0.000000  0.000000  0.000000  0.000000  0.000000
0.2500  0.000001  0.000000  0.000000  0.000000  0.000000
0.3750  0.000011  0.000001  0.000000  0.000000  0.000000
0.5000  0.000060  0.000009  0.000001  0.000000  0.000000
0.6000  0.000175  0.000031  0.000005  0.000001  0.000000
0.7000  0.000432  0.000089  0.000018  0.000004  0.000001
0.8000  0.000943  0.000222  0.000053  0.000013  0.000003
0.9000  0.001874  0.000498  0.000134  0.000036  0.000010
1.0000  0.003464  0.001025  0.000306  0.000092  0.000028
1.2000  0.010011  0.003572  0.001286  0.000465  0.000169
1.4000  0.024521  0.010253  0.004320  0.001829  0.000777
1.6000  0.053221  0.025537  0.012333  0.005981  0.002909
1.8000  0.105337  0.057072  0.031092  0.016998  0.009315
2.0000  0.193882  0.117119  0.071072  0.043254  0.026376
2.2000  0.336529  0.224328  0.150089  0.100655  0.067610
2.4000  0.556566  0.405930  0.296921  0.217584  0.159642
2.6000  0.884085  0.700485  0.556204  0.442243  0.351955
2.8000  1.357172  1.160987  0.994581  0.852796  0.731669
3.0000  2.023473  1.858976  1.709170  1.572200  1.446681
3.0120  2.070826  1.910357  1.763620  1.628912  1.504968
3.0240  2.119115  1.962979  1.819625  1.687496  1.565438
3.0360  2.168309  2.016792  1.877113  1.747850  1.627960
3.0480  2.218410  2.071798  1.936084  1.809976  1.692535
3.0600  2.269478  2.128098  1.996692  1.874091  1.759455
3.0720  2.321583  2.185811  2.059117  1.940448  1.829058
3.0840  2.374658  2.244821  2.123183  2.008801  1.901013
3.0960  2.428700  2.305127  2.188890  2.079148  1.975320
3.1080  2.483721  2.366745  2.256261  2.151523  2.052024
3.1200  2.539880  2.429951  2.325721  2.226536  2.131956
3.1320  2.597074  2.494565  2.396995  2.303791  2.214578
3.1440  2.655302  2.560588  2.470082  2.383289  2.299888
3.1560  2.714564  2.628019  2.544982  2.465029  2.387888
3.1680  2.774984  2.697074  2.622032  2.549501  2.479257
3.1800  2.836549  2.767726  2.701193  2.636650  2.573916
3.1920  2.899216  2.839907  2.782354  2.726314  2.671644
3.2040  2.962987  2.913616  2.865516  2.818494  2.772438
3.2160  3.026020  2.986718  2.948268  2.910525  2.873405
3.2280  3.085413  3.055846  3.026811  2.998207  2.969975
3.2400  3.143739  3.123985  3.104515  3.085265  3.066200
3.2566  3.222687  3.216639  3.210649  3.204697  3.198776
```

```
                         SODIUM
PERCENTAGE OF WAVEFUNCTION AT BOUNDARY L = 0 TO 4
.4439  .4544  .0935  .0076  .0004
NORMALIZED COEFFICIENTS  L = 0 TO 4
-.030305 -.080169  .057979  .023540 -.006947
            WAVEFUNCTION R(L) AT POSITION X
 X =  L=     0          1          2          3          4
0.0000  0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.0100  0.219978 -0.003491  0.000001  0.000000  0.000000
0.0200  0.391520 -0.013204  0.000010  0.000000  0.000000
0.0300  0.520497 -0.028096  0.000032  0.000000  0.000000
0.0400  0.612496 -0.047247  0.000072  0.000000  0.000000
0.0500  0.672602 -0.069857  0.000136  0.000001  0.000000
0.0600  0.705363 -0.095227  0.000226  0.000001  0.000000
0.0700  0.714831 -0.122754  0.000347  0.000002  0.000000
0.0800  0.704593 -0.151921  0.000501  0.000004  0.000000
0.0900  0.677818 -0.182282  0.000691  0.000006  0.000000
0.1000  0.637296 -0.213459  0.000917  0.000009  0.000000
0.2000 -0.114508 -0.521391  0.005493  0.000119  0.000004
0.3000 -0.864736 -0.758129  0.014664  0.000513  0.000027
0.4000 -1.326564 -0.897066  0.028389  0.001410  0.000104
0.5000 -1.489968 -0.943934  0.046270  0.003043  0.000287
0.6000 -1.415188 -0.915217  0.067851  0.005650  0.000657
0.7000 -1.173207 -0.829616  0.092781  0.009477  0.001317
0.8000 -0.826162 -0.704187  0.120877  0.014789  0.002401
0.9000 -0.422166 -0.552944  0.152166  0.021880  0.004077
1.0000  0.004589 -0.386577  0.186897  0.031089  0.006554
1.2000  0.846681 -0.035306  0.268436  0.057481  0.014987
1.4000  1.613077  0.318946  0.369153  0.097612  0.030401
1.6000  2.278904  0.666483  0.491641  0.155493  0.056379
1.8000  2.838874  1.003835  0.637220  0.235282  0.097425
2.0000  3.295214  1.329288  0.806662  0.341335  0.159050
2.2000  3.654388  1.642119  1.000682  0.478293  0.247892
2.4000  3.925073  1.942345  1.220085  0.651125  0.371813
2.6000  4.116951  2.230574  1.465837  0.865182  0.540046
2.8000  4.239440  2.507653  1.738952  1.126125  0.763210
3.0000  4.301550  2.774651  2.040569  1.440024  1.053527
3.0980  4.312480  2.902158  2.199137  1.615105  1.224433
3.1960  4.311803  3.027661  2.364990  1.805239  1.416568
3.2940  4.300370  3.151309  2.538289  2.011242  1.631816
3.3920  4.279005  3.273262  2.719209  2.233963  1.872184
3.4900  4.248511  3.393695  2.907948  2.474306  2.139846
3.5880  4.209620  3.512782  3.104705  2.733164  2.436998
3.6860  4.163074  3.630717  3.309709  3.011539  2.766146
3.7840  4.109518  3.747685  3.523190  3.310379  3.129694
3.8820  4.049639  3.863905  3.745424  3.630793  3.530496
3.9800  3.986397  3.975637  3.968521  3.961445  3.955010
3.9824  3.985653  3.976929  3.971123  3.965324  3.960018
```

```
NORMALIZED COEFFICIENTS  L = 5 TO 9
-.001759  .000469  .000098 -.000059  .000001
           WAVEFUNCTION R(L) AT POSITION X
 X =  L=     5          6          7          8          9
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.1250  0.000000  0.000000  0.000000  0.000000  0.000000
0.2500  0.000001  0.000000  0.000000  0.000000  0.000000
0.3750  0.000006  0.000000  0.000000  0.000000  0.000000
0.5000  0.000031  0.000003  0.000000  0.000000  0.000000
0.6000  0.000085  0.000012  0.000002  0.000000  0.000000
0.7000  0.000202  0.000032  0.000005  0.000001  0.000000
0.8000  0.000427  0.000079  0.000015  0.000003  0.000001
0.9000  0.000824  0.000173  0.000037  0.000008  0.000002
1.0000  0.001488  0.000350  0.000084  0.000020  0.000005
1.2000  0.004155  0.001185  0.000343  0.000100  0.000030
1.4000  0.009964  0.003345  0.001138  0.000390  0.000135
1.6000  0.021339  0.008241  0.003219  0.001266  0.000500
1.8000  0.041837  0.018278  0.008063  0.003578  0.001594
2.0000  0.076442  0.037284  0.018337  0.009065  0.004497
2.2000  0.131902  0.071071  0.038566  0.021021  0.011492
2.4000  0.217077  0.128090  0.076037  0.045306  0.027064
2.6000  0.343388  0.220292  0.142037  0.091870  0.059548
2.8000  0.525137  0.363967  0.253305  0.176746  0.123540
3.0000  0.780108  0.581009  0.434148  0.325076  0.243742
3.0490  0.856137  0.648495  0.492734  0.375111  0.285937
3.0980  0.938180  0.722535  0.558069  0.431820  0.334537
3.1470  1.026620  0.803660  0.630821  0.495986  0.390409
3.1960  1.121930  0.892546  0.711856  0.568641  0.454719
3.2450  1.224433  0.989663  0.801788  0.650534  0.528334
3.2940  1.334550  1.095625  0.901427  0.742656  0.612406
3.3430  1.452738  1.211109  1.011677  0.846132  0.708261
3.3920  1.579532  1.336922  1.133637  0.962353  0.817570
3.4410  1.715391  1.473773  1.268289  1.092588  0.941885
3.4900  1.860770  1.622365  1.416620  1.238123  1.082798
3.5390  2.016208  1.783548  1.579830  1.400541  1.242287
3.5880  2.182299  1.958263  1.759277  1.581658  1.422660
3.6370  2.359685  2.147558  1.956493  1.783564  1.626619
3.6860  2.548844  2.352213  2.172637  2.007864  1.856271
3.7350  2.750410  2.573282  2.409284  2.256749  2.114509
3.7840  2.965048  2.811878  2.668122  2.532603  2.404528
3.8330  3.193576  3.069392  2.951296  2.838505  2.730521
3.8820  3.436549  3.346789  3.260315  3.176660  3.095544
3.9310  3.694686  3.645319  3.597147  3.549953  3.503616
3.9800  3.948765  3.942592  3.936444  3.930297  3.924141
3.9824  3.954840  3.949696  3.944548  3.939378  3.934177
```

```
                                POTASSIUM
PERCENTAGE OF WAVEFUNCTION AT BOUNDARY L = 0 TO 4
.3862  .4750  .1301  .0079  .0005
NORMALIZED COEFFICIENTS  L = 0 TO 4
 .022954  .060856 -.044268 -.016977  .005510
           WAVEFUNCTION R(L) AT POSITION X
 X =  L=     0          1          2          3          4
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.0100 -0.272065  0.010820  0.000028  0.000000  0.000000
0.0200 -0.443649  0.039397  0.000213  0.000000  0.000000
0.0300 -0.535941  0.080738  0.000676  0.000000  0.000000
0.0400 -0.566349  0.130802  0.001511  0.000001  0.000000
0.0500 -0.549174  0.186328  0.002784  0.000002  0.000000
0.0600 -0.496115  0.244689  0.004543  0.000003  0.000000
0.0700 -0.416762  0.303783  0.006819  0.000006  0.000000
0.0800 -0.318947  0.361935  0.009628  0.000009  0.000000
0.0900 -0.209020  0.417784  0.012977  0.000014  0.000000
0.1000 -0.092159  0.470284  0.016861  0.000021  0.000000
0.2000  0.865541  0.738534  0.082218  0.000237  0.000004
0.3000  0.973988  0.576590  0.179959  0.000896  0.000026
0.4000  0.488137  0.186269  0.288547  0.002197  0.000092
0.5000 -0.204197 -0.260695  0.392051  0.004276  0.000236
0.6000 -0.855453 -0.665268  0.486642  0.007284  0.000509
0.7000 -1.357837 -0.988569  0.574207  0.011399  0.000974
0.8000 -1.676346 -1.217290  0.653123  0.016736  0.001703
0.9000 -1.815908 -1.353651  0.723050  0.023410  0.002782
1.0000 -1.801160 -1.408277  0.784945  0.031559  0.004312
1.2000 -1.431285 -1.325713  0.889986  0.052895  0.009211
1.4000 -0.787105 -1.065458  0.975648  0.081891  0.017510
1.6000 -0.028556 -0.699040  1.045608  0.119631  0.030562
1.8000  0.738218 -0.286318  1.115516  0.168701  0.050372
2.0000  1.464952  0.137595  1.202939  0.233022  0.079760
2.2000  2.133737  0.559218  1.314076  0.315951  0.121942
2.4000  2.733810  0.972116  1.447791  0.419980  0.180371
2.6000  3.260073  1.372278  1.602598  0.547628  0.259007
2.8000  3.711920  1.757357  1.777641  0.701637  0.362414
3.0000  4.091557  2.126186  1.972481  0.884942  0.495792
3.1950  4.395862  2.469799  2.181351  1.094850  0.660295
3.3900  4.639441  2.797703  2.408836  1.338577  0.864918
3.5850  4.826985  3.110348  2.655057  1.619294  1.116382
3.7800  4.963284  3.408390  2.920232  1.940328  1.422122
3.9750  5.053067  3.692648  3.204683  2.305162  1.790298
4.1700  5.101047  3.964155  3.508920  2.717522  2.229902
4.3650  5.111845  4.224108  3.833625  3.181435  2.750951
4.5600  5.089761  4.473802  4.179634  3.701098  3.364110
4.7550  5.039014  4.714691  4.547997  4.281176  4.081452
4.9500  4.963529  4.948310  4.939952  4.926698  4.916206
4.9593  4.959928  4.957910  4.956761  4.954944  4.953460
```

```
NORMALIZED COEFFICIENTS  L = 5 TO 9
 .002104 -.000878 -.000367  .000084  .000055
             WAVEFUNCTION R(L) AT POSITION X
 X =  L=    5          6          7          8          9
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.1250  0.000000  0.000000  0.000000  0.000000  0.000000
0.2500  0.000000  0.000000  0.000000  0.000000  0.000000
0.3750  0.000004  0.000000  0.000000  0.000000  0.000000
0.5000  0.000017  0.000001  0.000000  0.000000  0.000000
0.6000  0.000046  0.000005  0.000000  0.000000  0.000000
0.7000  0.000105  0.000013  0.000002  0.000000  0.000000
0.8000  0.000215  0.000030  0.000004  0.000001  0.000000
0.9000  0.000404  0.000064  0.000010  0.000002  0.000000
1.0000  0.000708  0.000125  0.000023  0.000004  0.000001
1.2000  0.001875  0.000407  0.000091  0.000021  0.000005
1.4000  0.004271  0.001099  0.000291  0.000078  0.000021
1.6000  0.008723  0.002604  0.000796  0.000247  0.000077
1.8000  0.016498  0.005611  0.001946  0.000683  0.000242
2.0000  0.029489  0.011252  0.004365  0.001711  0.000675
2.2000  0.050206  0.021231  0.009106  0.003940  0.001714
2.4000  0.081815  0.037972  0.017842  0.008446  0.004018
2.6000  0.128334  0.064860  0.033133  0.017037  0.008799
2.8000  0.194788  0.106505  0.058780  0.032628  0.018180
3.0000  0.287365  0.169047  0.100254  0.059753  0.035732
3.0970  0.343858  0.209215  0.128259  0.078995  0.048803
3.1940  0.409226  0.257258  0.162864  0.103553  0.066030
3.2910  0.484521  0.314394  0.205337  0.134649  0.088532
3.3880  0.570897  0.382004  0.257156  0.173756  0.117693
3.4850  0.669609  0.461633  0.320026  0.222617  0.155209
3.5820  0.782013  0.555000  0.395900  0.283296  0.203142
3.6790  0.909578  0.664026  0.487026  0.358232  0.263999
3.7760  1.053880  0.790826  0.595949  0.450268  0.340787
3.8730  1.216601  0.937718  0.725533  0.562685  0.437071
3.9700  1.399563  1.107280  0.879042  0.699323  0.557126
4.0670  1.604725  1.302348  1.060162  0.864628  0.706032
4.1640  1.834186  1.526037  1.273041  1.063729  0.889794
4.2610  2.090326  1.781972  1.522630  1.302903  1.115956
4.3580  2.375352  2.073584  1.813727  1.588381  1.392180
4.4550  2.691827  2.404939  2.152123  1.927830  1.728083
4.5520  3.042561  2.780588  2.544451  2.330230  2.135188
4.6490  3.430486  3.205383  2.997940  2.805592  2.626628
4.7460  3.858728  3.684605  3.520619  3.365271  3.217625
4.8430  4.330777  4.224262  4.121827  4.022765  3.926669
4.9400  4.850040  4.830348  4.811071  4.792108  4.773406
4.9593  4.952023  4.950596  4.949165  4.947722  4.946265
```

```
                              RUBIDIUM
PERCENTAGE OF WAVEFUNCTION AT BOUNDARY L = 0 TO 4
.4300  .3992  .1585  .0107  .0011
NORMALIZED COEFFICIENTS  L = 0 TO 4
 .021446  .051930 -.041076 -.018084  .007631
          WAVEFUNCTION R(L) AT POSITION X
 X =  L=    0          1          2          3          4
0.0000  0.000000 -0.000000  0.000000  0.000000  0.000000
0.0100  0.374993 -0.030107 -0.000464  0.000000  0.000000
0.0200  0.480943 -0.099987 -0.003291  0.000000  0.000000
0.0300  0.420869 -0.186502 -0.009875  0.000002  0.000000
0.0400  0.267222 -0.274274 -0.020847  0.000006  0.000000
0.0500  0.070167 -0.353463 -0.036326  0.000013  0.000000
0.0600 -0.136386 -0.418235 -0.056094  0.000025  0.000000
0.0700 -0.330332 -0.465590 -0.079729  0.000042  0.000000
0.0800 -0.498129 -0.494493 -0.106689  0.000067  0.000000
0.0900 -0.632326 -0.505217 -0.136379  0.000099  0.000000
0.1000 -0.729731 -0.498869 -0.168184  0.000140  0.000001
0.2000 -0.164920  0.098090 -0.488819  0.001162  0.000010
0.3000  0.969253  0.679262 -0.630104  0.003399  0.000052
0.4000  1.257737  0.777209 -0.569552  0.006785  0.000157
0.5000  0.810456  0.511360 -0.381592  0.011218  0.000365
0.6000  0.034220  0.080328 -0.133677  0.016650  0.000723
0.7000 -0.763965 -0.373678  0.129941  0.023119  0.001287
0.8000 -1.421652 -0.773809  0.385240  0.030746  0.002127
0.9000 -1.877747 -1.087949  0.621379  0.039683  0.003324
1.0000 -2.125006 -1.307706  0.833998  0.050040  0.004970
1.2000 -2.076007 -1.481748  1.183989  0.075277  0.010007
1.4000 -1.517137 -1.376176  1.442480  0.107216  0.018175
1.6000 -0.690428 -1.087580  1.628735  0.146935  0.030648
1.8000  0.228470 -0.694913  1.763922  0.195876  0.048901
2.0000  1.130734 -0.254284  1.868546  0.255998  0.074804
2.2000  1.960274  0.199768  1.959719  0.329731  0.110706
2.4000  2.697667  0.648447  2.054066  0.420433  0.159666
2.6000  3.337986  1.083006  2.159442  0.530955  0.225062
2.8000  3.880832  1.498845  2.278134  0.663628  0.310539
3.0000  4.330326  1.893983  2.411624  0.820950  0.420262
3.2220  4.728286  2.308063  2.578654  1.027770  0.576246
3.4440  5.030675  2.697460  2.766984  1.272391  0.775386
3.6660  5.248895  3.064200  2.978018  1.559205  1.026088
3.8880  5.393825  3.410697  3.213054  1.892902  1.337791
4.1100  5.475683  3.739583  3.473395  2.278590  1.721259
4.3320  5.503699  4.053590  3.760467  2.721713  2.188344
4.5540  5.486386  4.355553  4.075882  3.228273  2.752510
4.7760  5.431271  4.648256  4.421394  3.804744  3.428738
4.9980  5.345132  4.934560  4.799055  4.458221  4.233690
5.2200  5.239446  5.205528  5.192950  5.163128  5.141954
5.2292  5.235581  5.214497  5.206634  5.188043  5.174796
```

```
NORMALIZED COEFFICIENTS  L = 5 TO 9
 .003538 -.001551 -.000608  .000159  .000079
           WAVEFUNCTION R(L) AT POSITION X
 X =   L=     5           6           7           8           9
0.0000  0.000000   0.000000   0.000000   0.000000   0.000000
0.1250  0.000000   0.000000   0.000000   0.000000   0.000000
0.2500  0.000001   0.000000   0.000000   0.000000   0.000000
0.3750  0.000005   0.000000   0.000000   0.000000   0.000000
0.5000  0.000021   0.000002   0.000000   0.000000   0.000000
0.6000  0.000053   0.000005   0.000000   0.000000   0.000000
0.7000  0.000116   0.000012   0.000001   0.000000   0.000000
0.8000  0.000227   0.000028   0.000004   0.000001   0.000000
0.9000  0.000412   0.000058   0.000009   0.000001   0.000000
1.0000  0.000704   0.000112   0.000019   0.000003   0.000001
1.2000  0.001786   0.000352   0.000073   0.000015   0.000003
1.4000  0.003936   0.000926   0.000227   0.000057   0.000015
1.6000  0.007841   0.002151   0.000611   0.000177   0.000052
1.8000  0.014473   0.004543   0.001468   0.000483   0.000160
2.0000  0.025185   0.008909   0.003230   0.001188   0.000441
2.2000  0.041818   0.016467   0.006621   0.002695   0.001105
2.4000  0.066881   0.029015   0.012811   0.005716   0.002567
2.6000  0.103524   0.049051   0.023592   0.011448   0.005587
2.8000  0.155582   0.079931   0.041594   0.021809   0.011491
3.0000  0.227786   0.126123   0.070602   0.039778   0.022506
3.1110  0.278628   0.160454   0.093331   0.054611   0.032078
3.2220  0.338567   0.202483   0.122211   0.074165   0.045166
3.3330  0.408855   0.253592   0.158611   0.099698   0.062870
3.4440  0.490907   0.315398   0.204189   0.132795   0.086619
3.5550  0.586187   0.389632   0.260782   0.175265   0.118107
3.6660  0.696429   0.478403   0.330703   0.229463   0.159607
3.7770  0.823378   0.583910   0.416436   0.298003   0.213722
3.8880  0.969003   0.708699   0.520947   0.384091   0.283743
3.9990  1.135596   0.855828   0.647902   0.491820   0.373997
4.1100  1.325380   1.028345   0.801072   0.625524   0.489208
4.2210  1.540858   1.229769   0.984912   0.790451   0.635242
4.3320  1.784956   1.464325   1.204923   0.993270   0.819760
4.4430  2.060559   1.736284   1.466821   1.241097   1.051171
4.5540  2.370810   2.050411   1.777130   1.542255   1.339543
4.6650  2.719296   2.412276   2.143666   1.906961   1.697547
4.7760  3.109794   2.827873   2.575046   2.346760   2.139869
4.8870  3.546197   3.303515   3.080549   2.874374   2.683060
4.9980  4.032902   3.846466   3.671074   3.505066   3.347424
5.1090  4.574801   4.464976   4.359277   4.256968   4.157641
5.2200  5.122019   5.102610   5.083492   5.064566   5.045783
5.2292  5.162298   5.150102   5.138068   5.126133   5.114268
```

```
                           CESIUM
PERCENTAGE OF WAVEFUNCTION AT BOUNDARY L = 0 TO 4
.4221  .3484  .2091  .0170   .0026
NORMALIZED COEFFICIENTS  L = 0 TO 4
 .020835  .045154 -.039695 -.019735  .010166
            WAVEFUNCTION R(L) AT POSITION X
 X =  L=    0         1         2         3         4
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.0100 -0.372596  0.065131  0.001645  0.000002  0.000000
0.0200 -0.345210  0.196638  0.011018  0.000031  0.000000
0.0300 -0.139531  0.331602  0.031219  0.000139  0.000000
0.0400  0.114765  0.437397  0.062274  0.000389  0.000000
0.0500  0.346036  0.499815  0.102531  0.000842  0.000000
0.0600  0.518906  0.515773  0.149537  0.001552  0.000000
0.0700  0.620357  0.488594  0.200581  0.002561  0.000000
0.0800  0.650734  0.425020  0.253031  0.003901  0.000001
0.0900  0.617849  0.333232  0.304524  0.005591  0.000001
0.1000  0.533204  0.221659  0.353055  0.007638  0.000002
0.2000 -0.846746 -0.729235  0.487102  0.045256  0.000032
0.3000 -0.568557 -0.380403  0.084918  0.097672  0.000135
0.4000  0.549883  0.459747 -0.404650  0.145874  0.000350
0.5000  1.301278  1.031022 -0.729968  0.183801  0.000714
0.6000  1.388085  1.151565 -0.844668  0.211402  0.001267
0.7000  0.959286  0.907462 -0.784074  0.230088  0.002048
0.8000  0.262362  0.448857 -0.603456  0.241906  0.003104
0.9000 -0.495212 -0.091841 -0.354017  0.249257  0.004491
1.0000 -1.180555 -0.623711 -0.074032  0.254339  0.006283
1.2000 -2.107890 -1.479791  0.487545  0.264414  0.011450
1.4000 -2.394700 -1.968739  0.983413  0.279745  0.019412
1.6000 -2.164589 -2.114370  1.388400  0.302787  0.031101
1.8000 -1.594176 -1.996157  1.707859  0.335369  0.047683
2.0000 -0.838986 -1.699192  1.960111  0.379578  0.070657
2.2000 -0.010010 -1.292091  2.165496  0.437536  0.101874
2.4000  0.822083 -0.824105  2.342475  0.511524  0.143590
2.6000  1.616271 -0.327156  2.504515  0.603631  0.198401
2.8000  2.349822  0.178957  2.659908  0.715619  0.269165
3.0000  3.010814  0.681687  2.813846  0.849168  0.359058
3.2620  3.759615  1.322422  3.019537  1.059813  0.511742
3.5240  4.375416  1.933640  3.234728  1.314890  0.712389
3.7860  4.863033  2.509727  3.462155  1.618597  0.970957
4.0480  5.231623  3.048515  3.704178  1.975696  1.298870
4.3100  5.492982  3.550464  3.963345  2.391643  1.709090
4.5720  5.659925  4.017709  4.242262  2.872597  2.216426
4.8340  5.745401  4.453614  4.543763  3.425497  2.837617
5.0960  5.761954  4.862348  4.870911  4.058178  3.591742
5.3580  5.721049  5.248398  5.226837  4.779254  4.500196
5.6200  5.635690  5.608163  5.605461  5.578017  5.559490
5.6293  5.632469  5.618849  5.617483  5.603876  5.594662
```

```
NORMALIZED COEFFICIENTS  L = 5 TO 9
 .005365 -.002438 -.000949  .000248  .000118
           WAVEFUNCTION R(L) AT POSITION X
 X =  L=     5           6           7           8           9
0.0000 -0.000000 -0.000000 -0.000000 -0.000000 -0.000000
0.1250  0.000000  0.000000  0.000000  0.000000  0.000000
0.2500  0.000001  0.000000  0.000000  0.000000  0.000000
0.3750  0.000008  0.000000  0.000000  0.000000  0.000000
0.5000  0.000029  0.000002  0.000000  0.000000  0.000000
0.6000  0.000067  0.000005  0.000000  0.000000  0.000000
0.7000  0.000135  0.000012  0.000001  0.000000  0.000000
0.8000  0.000250  0.000026  0.000003  0.000000  0.000000
0.9000  0.000431  0.000052  0.000007  0.000001  0.000000
1.0000  0.000705  0.000097  0.000014  0.000002  0.000000
1.2000  0.001675  0.000288  0.000053  0.000010  0.000002
1.4000  0.003530  0.000732  0.000161  0.000037  0.000009
1.6000  0.006797  0.001657  0.000425  0.000112  0.000030
1.8000  0.012212  0.003426  0.001003  0.000301  0.000092
2.0000  0.020793  0.006607  0.002176  0.000732  0.000249
2.2000  0.033906  0.012039  0.004408  0.001643  0.000619
2.4000  0.053345  0.020936  0.008436  0.003452  0.001426
2.6000  0.081390  0.034987  0.015386  0.006856  0.003081
2.8000  0.120833  0.056461  0.026906  0.012969  0.006297
3.0000  0.175078  0.088359  0.045360  0.023520  0.012274
3.1310  0.220558  0.116717  0.062733  0.034026  0.018565
3.2620  0.275449  0.152513  0.085647  0.048499  0.027610
3.3930  0.341252  0.197321  0.115576  0.068211  0.040455
3.5240  0.419582  0.252921  0.154255  0.094732  0.058438
3.6550  0.512230  0.321353  0.203757  0.130008  0.083289
3.7860  0.621188  0.404982  0.266572  0.176466  0.117246
3.9170  0.748682  0.506541  0.345690  0.237127  0.163198
4.0480  0.897136  0.629110  0.444593  0.315644  0.224764
4.1790  1.069181  0.776139  0.567320  0.416389  0.306426
4.3100  1.267731  0.951576  0.718639  0.544693  0.413821
4.4410  1.496003  1.159906  0.904137  0.707009  0.553998
4.5720  1.757500  1.406159  1.130278  0.911030  0.735626
4.7030  2.055964  1.695857  1.404360  1.165705  0.969083
4.8340  2.395539  2.035273  1.734901  1.481762  1.267167
4.9650  2.780750  2.431435  2.131707  1.871906  1.645461
5.0960  3.216538  2.892221  2.606072  2.351170  2.122921
5.2270  3.708086  3.426098  3.170446  2.936571  2.721572
5.3580  4.261118  4.042629  3.839232  3.648269  3.468160
5.4890  4.881848  4.752421  4.628780  4.509715  4.394568
5.6200  5.542639  5.526401  5.510496  5.494803  5.479262
5.6293  5.586263  5.578156  5.570200  5.562338  5.554540
```

APPENDIX C

```
$JOB           000109 VANDERHOFF IS FINISHED
$IBJOB         NODECK
$IBFTC NI 2
  335  FORMAT(35H- VALUE OF LEGENDRE INTEGRATION
   31  FORMAT (1H ,10F13.8)
 1965  FORMAT (I2,F20.8 )
 5105  FORMAT( I2)
 1331  FORMAT(1H-,          I3     )
  885  FORMAT (30H- POTENTIAL EQ.                     ///)
   11  FORMAT (1H1,28HVALUE OF W-S SPHERE RADIUS   , F20.8///)
 4111  FORMAT(F20.8)
  887  FORMAT(30H- ENERGY VALUE EQ.
  886  FORMAT (1H ,F20.8/////)
  336  FORMAT(30H-  MATRICS ELEMENTS                            ///)
   61  FORMAT  (1H ,10F13.8)
    8  FORMAT(1H-,18H DETERMINATE=       ,  E20.8)
 1861  FORMAT(1H0,8HPF VALUE             ,E20.8  )
1888   FORMAT(1H0,40HNORMALIZED WAVE FUNCTION COEFFICIENTS          ,////)
 1889  FORMAT(1H ,10F13.8)
    1  FORMAT(1H ,14X,F8.3,9X,F8.3,16H KOHN,S SECOND         )
    2  FORMAT(1H ,14X,F8.3,9X,F8.3,16H RA = 1                )
 6005  FORMAT(15H0ACCURACY CHECK ,F8.3,9HFOR ANGLE  ,F8.3 )
 6010  FORMAT(40H0A(L) = C(L)*SQRTN(L) BELOW A(L) SQ                ,///)
       DIMENSION P(20,20)
       DIMENSION EIBV(5),DVTC(5)
       DIMENSION AANN(20)
       DIMENSION A(20,20)
       DIMENSION CAB(401), COFL(20)
       DIMENSION VV(4),GG(4)
        DIMENSION RA(20)
       DIMENSIONH(10),R(401),V(401),C(20),DP(20),B(401)
       DIMENSION PP(20),ZXY(4)
       DIMENSION COOL(20)
         COMMON  T, E, H1
        COMMON NUM
C      FORM IS A LAGRANGIAN INTERPOLATION OF ORDER 3
     0FORM(X,X0,X1,X2,X3,F0,F1,F2,F3)=(X-X1)*(X-X2)*(X-X3)*F0/((X0-X1
     1)*(X0-X2)*(X0-X3))+(X-X0)*(X-X2)*(X-X3)*F1/((X1-X0)*(X1-X2)*(X1-
     2X3))+ (X-X0)*(X-X1)*(X-X3)*F2/((X2-X0)*(X2-X1)*(X2-X3))+(X-X0)*
     3(X-X1)*(X-X2)*F3/((X3-X0)*(X3-X1)*(X3-X2))
C      READ IN  LEGENDRE INTEGRAL
       WRITE (6,335)
       DO 41 I=1,20
       READ(5)(P(I,N),N=1,20)
       WRITE(6,31)(P(I,N), N=1,10 )
       WRITE(6,31)(P(I,N), N=11,20)
41     CONTINUE
C      VAKF,NZ,DUMB ARE VALENCE NUMBER,ATOMIC NUMBER,AND LATTICE CONSTANT
       READ(5,4111)  VAKF
       READ (5,1965) NZ,DUMB
       F=1000.
```

```
C       NUM IS THE DIMENSION OF THE MATRIX
        READ (5,5105)  NUM
        WRITE (6,1331)         NUM
        PI= 3.14159265
        KI=40
        I91=401
        H(1)=.0025
        DO 29  K= 2,10
29      H(K) =H(K-1)*1.80
        Z=NZ
        AMU=.88534138/Z**.33333333
C       READ IN POSITION AND POTENTIAL OF ELEMENT DESIRED
        READ(5) (R(K),V(K),K=1,I91)
        WRITE (6,885)
        I9=I91-1
C       PRINTS OUT VALUES OF V AND R
        CALL SNAFU(   V,R     )
        V0= (V(1)-V(2))/(R(2)-R(1))
        V(1)=0.0000
        DO27 I=2,I91
        B(I) =V(I)
27      V(I)= 0.0000
        Z2 = Z*Z
        R2=R(2)*R(2)
        R3=R2*R(2)
        GG(1) = 0.0
        GG(2) = 0.4
        GG(3) = (2./3.)
        GG(4) = 0.8
        DD=(DUMB/.529172)*(3.0/(8.*PI))**.33333333
        WRITE(6,11)    DD
        READ(5,4111) EIBV(1)
        READ(5,4111) EIBV(2)
        READ(5,4111) EIBV(3)
        READ(5,4111) EIBV(4)
        DO 888 KILL = 1,5
        E = EIBV (KILL)
        WRITE (6,887)
        WRITE (6,886)  E
        CAB(1) = 0.0
        APVE = E
        DO 20 L= 1,NUM
        IJK =0
        T=L-1
        LL= T
        E = APVE
```

```
      ALP= (2.* Z2-(T+1.)*(2.*V0-E))/(2.*(2.*T+3.)*(T+1.))
      BET=  Z*(2.* Z2-(3.*T+4.)*(2.*V0-E))/(6.*(T+1.)*(T+2.)*(2.*T+3.))
      C(L)=F*(R(2)**(T+1.))*(1.-( Z*R(2))/(T+1.)+ALP*R2-BET*R3)
      V(2)= C(L)
      CAB(2) = C(L) *C(L)
      DP(L)=F*(T+1.)*(R(2)**T)+F*(R(2)**(T+1.))*(-( Z*(T+2.))/(T+1.)
     1    +ALP*R(2)*(T+3.)-BET*R2*(T+4.))
      E=-E
      KJ = KI
      K= 1
      DO 16J=1,10
      H1=H(J)*AMU
      DO76   JJ=1,KJ
      K=K+1
      IF (R(K+1).GT.DD) GO TO 2888
      GO TO 2777
2888  IJK = IJK +1
      IF (IJK.GT.1) GO TO 999
      BBB=B(K+1)
      BRB = R(K+1)
     0 B(K+1) = FORM(DD ,R(K-1),R(K),R(K+1),R(K+2),B(K-1),B(K),B(K+1),
     1          B(K+2))
      H1=DD-R(K)
      R(K+1) = R(K) +H1
2777  CONTINUE
      DO 1076  KAT = 1,4
      XXX  = R(K) + GG(KAT)*(R(K+1)-R(K))
     0 VV(KAT)= FORM(XXX,R(K-1),R(K),R(K+1),R(K+2),B(K-1),B(K),B(K+1),
     1          B(K+2))
      VV(KAT) = VV(KAT)/XXX
1076  CONTINUE
      VA = VV(1)
      VB = VV(2)
      VC = VV(3)
      VD = VV(4)
C     TVP IS A RUNGE KUTTA NYSTROM SUBROUTINE FOR DIFF. EQ.
      CALL TVP(C(L),DP(L),R(K),VA,VB,VC,VD,W,DW)
      V(K+1)= W
      CAB(K+1) = W*W
      KKK=K+1
      DP(L)=DW
      C(L)=W
      RATIO =DW/W
      IF(IJK.NE.1) GO TO 1057
      B(K+1) = BBB
      R(K+1) = BRB
1057  CONTINUE
      IF(KKK.EQ.41) GO TO 16
76    CONTINUE
16    CONTINUE
999   RA(L)=(10./DD)*(DD*RATIO-1.)
```

```
        IAK = 0
        DO 202  IYUP = 1,401
        IAK = IAK +1
        IF(R(IYUP).GT.DD)  GO TO 203
        CAB(IAK) = CAB(IAK)*DD*DD/(W*W)
        V(IAK)=(V(IAK)*DD/W)
202     CONTINUE
203     CAB(IAK) = CAB(IAK)*DD*DD/(W*W)
        V(IAK)=(V(IAK)*DD/W)
        IF(L.EQ.1) S=F*(DD/W)
C       SUBROUTINE SIMP IS A SIMPSON INTEGRATION
        AANN(L) = ((4.*PI)/((2.*T)+1.))*SIMP(CAB,R,DD)
C       PRINTS OUT VALUES OF V AND R
        CALL SNAFU(V,R)
20      CONTINUE
        DO 72 I=1,NUM
        DO 72 J=1,NUM
        A(I,J) = P(I,J)*(RA(I)+RA(J))
        JT = I+J
        J2T = JT/2
        J3T=2*J2T
        IF(J3T.NE.JT) GO TO 71
        IT= I/2
        I2T= 2*IT
        IF(I2T.EQ.I)  GO TO 71
        GO TO 72
71      A(I,J)=-A(I,J)
  72    CONTINUE
C       A IS COEFFICIENT  OF HOMOGENEOUS EQUATIONS
        WRITE (6,336)
        DO 761  I= 1,NUM
        WRITE(6,61)  (A(I,J), J=1,10)
        WRITE(6,61)  (A(I,J), J=11,NUM)
761     CONTINUE
        NUMB = NUM
C       DET IS A SUBROUTINE WHICH GIVES THE DETERMINATE VALUE
        COD  = DET(A,NUMB)
        DVTC(KILL) = COD
        WRITE (6,8)   COD
C       SUBROUTINE CRAM SOLVES HOMOGENEOUS EQUATIONS
        CALL CRAM( A,COFL)
        TUM = 0.0
        DO 1776 IPUP = 1,NUM
        TUM = TUM + COFL(IPUP)*AANN(IPUP)*COFL(IPUP)
1776    CONTINUE
        FANS = (COFL(1)*COFL(1) *S*S)/TUM
        WRITE (6,1861)  FANS
C       INTERPOLATION OF NEW ENERGY VALUE
      0 IF(KILL.EQ.4)EIBV(5) = FORM(0.,DVTC(1) ,DVTC(2) ,DVTC(3) ,DVTC
      1 (4) ,EIBV(1) ,EIBV(2) ,EIBV(3) , EIBV(4))
        DO 1887 JACK =1,NUM
        COFL(JACK) = COFL(JACK)/SQRT(TUM)
1887    CONTINUE
        WRITE(6,1888)
        WRITE(6,1889) (COFL(JOCK),JOCK=1,10)
        WRITE(6,1889) (COFL(JOCK),JOCK=11,NUM)
        IF(NUM.LT.2) GO TO 6004
```

```
C     CHECK OF BOUNDARY CONDITIONS
      ZXY(1) = 30.
      ZXY(2) = 60.
      ZXY(3) = 75.
      ZXY(4) = 0.0
      DO 6006 IZY =1,4
      XYZ = ZXY(IZY)*PI/180.
      XYZ =COS(XYZ)
      PP(1) =1.
      PP(2) =XYZ
      DO 6001 IY =3,NUM
      AIY = IY - 1
      PP(IY)=((2.*AIY-1.)*XYZ*PP(IY-1)-(AIY-1.)*PP(IY-2))/AIY
6001  CONTINUE
      NUMM = NUM + 1
      DO 6002 IY = NUMM ,20
      PP(IY) = 0.0
6002  CONTINUE
    0 CHE1=(COFL(20)*PP(20)+COFL(18)*PP(18)+COFL(16)*PP(16)+COFL(14)*
    1 PP(14)+COFL(12)*PP(12)+COFL(10)*PP(10)+COFL(8)*PP(8)+COFL(6)*
    2 PP(6)+COFL(4)*PP(4)+COFL(2)*PP(2))
    0 CHE2 =
    1 (COFL(19)*PP(19)+COFL(17)*PP(17)+COFL(15)*PP(15)+COFL(13)*PP(13)
    2 +COFL(11)*PP(11)+COFL(9)*PP(9)+COFL(7)*PP(7)+COFL(5)*PP(5) +
    3 COFL(3)*PP(3)+COFL(1)*PP(1))
    0 CCHE1=(COFL(20)*PP(20)*RA(20)+COFL(18)*PP(18)*RA(18)+COFL(16)*
    1PP(16)*RA(16)+COFL(14)*PP(14)*RA(14)+COFL(12)*PP(12)*RA(12)+
    2 COFL(10)*PP(10)*RA(10)+COFL(8)*PP(8)*RA(8)+COFL(6)*PP(6)*RA(6)+
    3 COFL(4)*PP(4)*RA(4)+COFL(2)*PP(2)*RA(2))
    0 CCHE2=(COFL(19)*PP(19)*RA(19)+COFL(17)*PP(17)*RA(17)+
    1 COFL(15)*PP(15)*RA(15)+COFL(13)*PP(13)*RA(13)+COFL(11)*PP(11)*
    2 RA(11) +COFL(9)*PP(9)*RA(9)+COFL(7)*PP(7)*RA(7)+COFL(5)*PP(5)
    3 *RA(5)+COFL(3)*PP(3)*RA(3)+COFL(1)*PP(1)*RA(1))
      VANDE=((9.*PI*VAKF/4.)**.33333333)*XYZ
      WAAM = (CHE1/CHE2)/TAN(VANDE)
      WAAM1=(CHE1/CHE2)*TAN(VANDE)
      WAAM2=(CCHE1/CCHE2)*TAN(VANDE)
      WRITE (6,6005)          WAAM , ZXY(IZY)
      WRITE(6,1) WAAM2,ZXY(IZY)
      WRITE(6,2) WAAM1,ZXY(IZY)
6006  CONTINUE
6004  CONTINUE
      DO 6011 MAN = 1,NUM
      COOL(MAN) = COFL(MAN)*COFL(MAN)*AANN(MAN)
6011  CONTINUE
      WRITE (6,6010)
      WRITE(6,1889) (COOL(NAM),NAM=1,10)
      WRITE(6,1889) (COOL(NAM),NAM=11,NUM)
888   CONTINUE
      STOP
     END
```

```
$IBFTC  GIJ
      SUBROUTINE SNAFU (  V, R)
      DIMENSION V(401),R(401)
      I91 = 401
      I9 = I91- 1
      DO116 J=1,I9,10
      J9=J+9
116   WRITE(6,40) R(J),(V(K),K=J,J9)
      WRITE(6,40) R(I91),V(I91)
  40  FORMAT (1X,F10.6,1X,10E12.5)
      RETURN
      END
$IBFTC  4
      FUNCTION DET (ZIP,NUM )
      DIMENSION ZIP(20,20)
       DIMENSION A(20,20),D(20),ZZ(20,20),BB(20,20)
      DO 17 I = 1,NUM
      DO 17 J =1,NUM
      A(I,J) = ZIP(I,J)
17    CONTINUE
      N1 = NUM -1
      DO 6 L=1,N1
      N= N1+2 -L
      KK=0
      DO12 J=2,N
      IF(ABS(A(1,1)).LE.0.00000009) GO TO 10
      IF (ABS(A(1,1)).GE.ABS(A(J,1)))   GO TO12
   10 KK=KK+1
      DO 2 K=1,N
     ZZ(J,K)=A(J,K)
      A(J,K)=A(1,K)
      A(1,K)=ZZ(J,K)
    2 CONTINUE
12    CONTINUE
      D(L)=A(1,1)
      DO 3 K=1,N
      A(1,K)=A(1,K)/D(L)
    3  CONTINUE
      DO 4 K=2,N
      DO 4 M=2,N
     BB(K,M)=A(K,M)-A(1,M)*A(K,1)
    4 CONTINUE
      DO 5 K=2,N
      DO 5 M=2,N
    5 A(K-1,M-1)=BB(K,M)
      K1=KK/2
      K2=2*K1
      IF(KK.NE.K2)   D(L)=-D(L)
    6 CONTINUE
      DO 7 L=1,N1
    7  A(1,1)=A(1,1)*D(L)
      DET = A(1,1)
      RETURN
      END
```

```
$IBFTC 8SUBROUTINE TVP(Y,DY,R,VA,VB,VC,VD,Z,DZ)
      DIMENSION V(4),U(4)
         COMMON  T, E, H1
      V(1)=VA
      V(2)=VB
      V(3)=VC
      V(4)=VD
      R2=R+0.4*H1
      R3=R+(2.0/3.0)*H1
      R4=R+0.8*H1
   23 U(1)=V(1)+T*(T+1.0)/(R*R)-E
       U(2)=V(2)+T*(T+1.0)/(R2*R2)-E
       U(3)=V(3)+T*(T+1.0)/(R3*R3)-E
      U(4)=V(4)+T*(T+1.0)/(R4*R4)-E
      A1=H1*Y*U(1)
      Q1=H1*(DY+A1/5.0)
      Q2=H1*(DY+A1/3.0)
      A2=H1*(Y+0.4*Q1)*U(2)
      A3=H1*(Y+2.0*Q2/3.0)*U(3)
      Q3=H1*(DY+(A1+A2)/5.0)
      A4=H1*(Y+0.8*Q3)*U(4)
      Z=Y+H1*(DY+(23.*A1+75.*A2-27.*A3+25.*A4)/192.0)
      DZ=DY+(23.*A1+125.*A2-81.*A3+125.*A4)/192.0
      RETURN
      END
$IBFTC  3
       SUBROUTINE CRAM(A,ANS)
         COMMON  T, E, H1
       COMMON NUM
       DIMENSION A(20,20),ANS(20),Z(20)
       NU2 = NUM -1
       DEL = DET(A,NU2)
       DO 1 J = 1,NU2
       DO 2 I = 1,NUM
       Z(I) = A(I,J)
       A(I,J) = -A(I,NUM)
2      CONTINUE
       DEL2 = DET(A,NU2)
       ANS(J) = DEL2/DEL
       DO 3 I=1,NUM
       A(I,J) =   Z(I)
3      CONTINUE
1      CONTINUE
       ANS(NUM ) = 1.
       RETURN
       END
```

```
$IBFTC  2
      FUNCTION SIMP ( V,R,R1)
      DIMENSION V(401), R(401)
     0DORM(Y,Y0,Y1,Y2,P0,P1,P2 ) = (Y-Y1)*(Y-Y2)*P0/((Y0-Y1)*(Y0-Y2))+
     1   (Y-Y0)*(Y-Y2)*P1/((Y1-Y0)*(Y1-Y2))+(Y-Y0)*(Y-Y1)*P2/((Y2-Y0)
     2      *(Y2-Y1))
      SUM  = 0.0
      IJK = 0
      DO 1  K = 1,401
      IF(R(K+1).GT.R1.OR.R(K+1).EQ.R1)  GO TO 2
      GO TO 3
2     CONTINUE
      IJK = IJK +1
      IF ( IJK.GT.1) GO TO 4
      RR = R(K+1)
      VV = V(K+1)
      V(K+1)= DORM(R1,R(K),R(K+1),R(K+2),V(K),V(K+1),V(K+2))
      R(K+1 ) = R1
3     Q = ((R(K+1)-R(K))/2.) + R(K)
      FQ= DORM(Q,      R(K),R(K+1),R(K+2),V(K),V(K+1),V(K+2))
      AQ = ((R(K+1)-R(K))/6.)*(V(K) +4.*FQ +V(K+1))
       SUM = AQ+ SUM
1     CONTINUE
4     SIMP = SUM
      R(K) = RR
      V(K) = VV
      RETURN
      END
$ENTRY
$IBSYS
```

```
$JOB           000109 VANDERHOFF LEGENDRE
$IBJOB         NODECK
$IBFTC LEGDRE
C      EVALUATION OF THE INTEGRAL OF THE PRODUCT OF TWO LEGENDRE
C      POLYNOMIALS MULT. BY A PHASE FACTOR
       DIMENSION  R(801),H(10),PP(801,20),V(801),P(20,20)
       COMMON R,H,KI,I51,C
       I51  = 801
         KI = 100
       C=1.
      PI = 3.14159265
       A =2.*1.9192
       H(1)=.00125
       DO 1001  N=2,10
1001   H(N) = H(N-1)
       R(1) = 0.0
       DO 1002   L= 2,801
1002   R(L)= R(L-1) +H(1)
       DO 1008  L=1,801
       PP(L,1) = 1.
       PP(L,2) = R(L)
       DO 1008  IX = 3,20
       AIY =IX-1
       PP(L,IX)=((2.*AIY-1.)*R(L)*PP(L,IX-1)-(AIY-1.)*PP(L,IX-2))/AIY
1008   CONTINUE
       DO 1003 I =1,20
       DO 1003 J =1,20
       DO 1009  L=1,801
       V(L)= PP(L,I)*PP(L,J)
1009    CONTINUE
       II=I+J
       IJ=II/2
       I2J=2*IJ
       NI = 1
       IF (I2J.EQ.II)  NI = 2
       CALL FILON (V(L),A,P(I,J),NI)
       P(I,J) = 2.*P(I,J)
       IF (NI.EQ. 1)  P(I,J) = - P(I,J)
1003   CONTINUE
       WRITE (6,335)
335    FORMAT(35H- VALUE OF LEGENDRE INTEGRATION                   ///)
       DO 41 I=1,20
       WRITE(7) (P(I,N),N=1,20)
41     CONTINUE
        STOP
        END
```

```
$IBFTC FILON
      SUBROUTINE FILON (Y,Q,F,N)
C IF N=1,F IS THE INTEGRAL OF Y(SIN(QR),OTHERWISE F IS THE INTEGRAL OF Y*CO
       DIMENSION Y(801),H(10),R(801)
      COMMON R,H,KI,I51,C
      NH=I51/KI
      KI2=KI/2
      F=0.
      I=0
      DO 1 J=1,NH
      F1=Y(I+1)*SIN(Q*R(I+1))
      IF (N.EQ.1) F1=-Y(I+1)*COS(Q*R(I+1))
      C1=0.
      C2=0.
      DO 2 K=1,KI2
      I=I+2
      IF (N.EQ.1) GO TO 10
      C1=C1+Y(I+1)*COS(Q*R(I+1))
      IF (K.EQ.1) C1=C1+Y(I-1)*COS(Q*R(I-1))/2.
      IF (K.EQ.KI2) C1=C1-Y(I+1)*COS(Q*R(I+1))/2.
      C2=C2+Y(I)*COS(Q*R(I))
      GO TO 2
   10 C1=C1+Y(I+1)*SIN(Q*R(I+1))
      IF (K.EQ.1) C1=C1+Y(I-1)*SIN(Q*R(I-1))/2.
      IF (K.EQ.KI2) C1=C1-Y(I+1)*SIN(Q*R(I+1))/2.
      C2=C2+Y(I)*SIN(Q*R(I))
    2 CONTINUE
      F2=Y(I+1)*SIN(Q*R(I+1))
      IF (N.EQ.1) F2=-Y(I+1)*COS(Q*R(I+1))
      Z=H(J)*Q*C
      IF (Z.LT..2) GO TO 3
      W=COS(Z)
      X=SIN(Z)
      A=(Z*Z+Z*X*W-2.*X*X)/(Z*Z*Z)
      B=2.*(Z*(1.+W*W)-2.*X*W)/(Z*Z*Z)
      D=4.*(X-Z*W)/(Z*Z*Z)
      GO TO 1
    3 A=Z*Z*Z*(2./45.-2.*Z*Z*(1./315.-Z*Z/4725.))
      B=2./3.+Z*Z*(2./15.+2.*Z*Z*(-2./105.+Z*Z/567.))
      D=4./3.+Z*Z*(-2./15.+Z*Z*(1./210.-Z*Z/11340.))
    1 F=F+H(J)*(A*(F2-F1)+B*C1+D*C2)*C
      RETURN
      END
$ENTRY
$IBSYS
```

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