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NON-ADIABATICITY CORRECTIONS TO THE BORN-OPPENHEIMER
APPROXIMATION WITH CALCULATIONS FOR MESIC
AND ELECTRONIC HYDROGEN MOLECULAR IONS
(Thesis)

M. R. Patterson

R. L. Becker

Adapted from a dissertation presented to the Graduate Council of the University of Tennessee in partial fulfillment of the requirements for the degree of Doctor of Philosophy by M. R. Patterson.

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APPROXIMATION WITH CALCULATIONS FOR MESIC
AND ELECTRONIC HYDROGEN MOLECULAR IONS

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R. L. Becker, Physics Division, ORNL

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AUGUST 1967

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ABSTRACT

For generalized hydrogen molecular ions the adiabatic approximation is excellent if $\epsilon/4$, the ratio of the mass m_3 of the binding particle to the total mass, is small (e.g., H_2^+). For $(p\mu p)^+$, $\epsilon = 0.213$, the large mass ratio introduces correction terms to the adiabatic approximation. A detailed formalism using rotation matrices and exact two-center "electronic" functions was worked out. The non-adiabatic corrections take the form of couplings between different electronic states. Coupled radial equations involving as many as six electronic states have been solved for ground and excited states of $(p\mu p)^+$, $(d\mu d)^+$, $(t\mu t)^+$, $(\mu e \mu)^+$, and $(pep)^+$.

The resultant wave functions were used to calculate the probability 2γ that the lepton and either nucleus coincide. For ortho $(p\mu p)^+$ a new upper limit is $2\gamma_0 = 1.12$, as compared to the adiabatic value $2\gamma_0 = 1.165$. Variational calculations supply the lower limit $2\gamma_0 = 1.00$. Using the value $2\gamma_0 = 1.12$, the weak interaction coupling constants for muon capture in hydrogen are consistent with those for muon capture in He^3 and Ca^{40} at the axial vector coupling constant values $g_A^{(\mu)}/g_V^{(\beta)} = -1.26 \begin{Bmatrix} +0.05 \\ -0.04 \end{Bmatrix}$ and the induced pseudoscalar coupling constant values $g_p^{(\mu)}/g_A^{(\mu)} = 16.2 \pm 3.2$.

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CHAPTER I

INTRODUCTION

Muon capture experiments using bubble chambers have lead to a great interest in the mu-mesic hydrogen molecular ions, $(H\mu H)^+$, formed by many of the incident muons (Rubbia, 1964). In particular, the probability density of a muon at a hydrogen nucleus must be available from a molecular calculation in order to obtain a theoretical capture rate for the weak interaction $\mu + p \rightarrow n + \nu$. This probability density, called the overlap, has previously been calculated by two methods: (1) variational calculations using many terms in the trial function and (2) adiabatic approximations which include the first order correction to the Born-Oppenheimer approximation. The present work consists of an attempt to generalize the adiabatic approximation to include the higher order corrections made necessary by the large mass ratio of mu mesic hydrogen molecular ions. This independent evaluation of the overlap was then used to obtain limits on the weak interaction coupling constants. Other physical quantities, such as the binding energy, were obtained for the molecular systems studied.

The hydrogen molecular ion consists of two separated hydrogen nuclei, such as protons, deuterons, or tritons, and a negative lepton. This three-body system is bound by Coulomb forces, attraction of the lepton by both nuclei being sufficient to balance the mutual repulsion of the nuclei. The ordinary hydrogen molecular ion consists of two protons and an electron, $(pep)^+$, and has been studied since the early days of quantum mechanics.

The relative simplicity of the hydrogen molecular ion makes it of great interest. It serves as the prototype of all diatomic molecules, and the theoretical techniques evolved to treat it have been applied to molecular systems of many different types. In short, it is the intermediate step between the two-body problem, which can be solved exactly, and the many-body problem, which must be approximated.

It had been found in classical mechanics that a restricted three-body system, having two centers fixed, could be solved exactly (Pauli, 1922, and Whittaker, 1927). After the invention of quantum mechanics, it was suspected that exact quantum mechanical solutions for the clamped nuclei problem might be found, because of the correspondence of classical and quantum solutions of simple systems such as the hydrogen atom. Burrau (1927) separated variables in the quantum clamped nuclei problem and numerically integrated the ordinary differential equations. Guillemin and Zener (1929) and Teller (1930) applied variational calculations to this problem. Hylleraas (1931) and Jaffé (1934) were successful in obtaining exact solutions.

Bates, Ledsham, and Stewart (1953) combined the results of Stratton et al. (1941) with those of Jaffé (1934) to obtain exact solutions for a hydrogen molecular ion having the two nuclei clamped at a constant separation. Such a solution, representing motion of the lepton at a fixed internuclear separation, will be referred to below as an electronic state. Bates, Ledsham, and Stewart (1953) provide accurate values of the electronic energies and the electronic wave functions as a function of the internuclear separation distance. Further references to work on the electronic states may be found in Wallis and Hulbert (1954).

The Born-Oppenheimer approximation (Born and Oppenheimer, 1928a, 1928b) provides a means by which the motion of the nuclei may be considered. The more massive nuclei move with a smaller dominant vibrational frequency than the lepton and may, to first order in the mass ratio, be regarded as moving in the average potential generated by the lepton. Since the mass of a muon is about 200 times larger than that of an electron, the ratio of the dominant nuclear vibrational frequency to the muon orbital frequency is about 14 times larger than the corresponding ratio for an electronic ion. The Born-Oppenheimer approximation must be generalized to include coupling between these motions. Application of the Born-Oppenheimer approximation is discussed by Messiah (1962) and many other authors.

The lowest order (adiabatic) coupling was first studied by Van Vleck (1936). Further investigation of the coupling has been done by Dalgarno and McCarroll (1956); Wu, Rosenberg, and Sandstrom (1960); Cohen, Judd and Riddell (1960a); Jepsen and Hirshfelder (1960); and Laurenzi and Fitts (1965). The calculation by Cohen, Judd, and Riddell (1960a) obtained adiabatic coupling terms from two variational electronic wave functions. One adiabatic equation, containing approximate electronic energies, was solved for the motion of the nuclei in the homonuclear case; and two coupled equations were solved in the heteronuclear case.

Laurenzi and Fitts (1965) used the exact electronic wave functions of Bates, Ledsham, and Stewart (1953) to calculate coupling terms between the electronic ground state and four higher states. Laurenzi and Fitts

(1965) attempted to reduce the magnitude of the coupling terms by employing a different coordinate system than that of Cohen, Judd, and Riddell (1960a). The reader is also directed to the work of Belyaev et al. (1960), Marschall and Schmidt (1957), Jackson (1957), Skyrme (1957), and Johnson (1941) for other adiabatic treatments of hydrogen molecular ions. Zel'dovich and Gershtein (1961) review much of the earlier work on $(\text{H}\mu\text{H})^+$ ions in an article concerning nuclear catalysis. Slater (1963) devotes a chapter to a description of $(\text{pep})^+$.

Variational calculations have been reported by several authors and are referenced by Carter (1966). Kolos, Roothaan, and Sack (1960) demonstrated that a trial function which worked well for $(\text{p}\mu\text{p})^+$ did not do so well for $(\text{pep})^+$. The work of Flüge and Schröder (1961), Fröman and Kinsey (1961), Scherr and Machacek (1964), Wessel and Phillipson (1964), Halpern (1964b), Frost (1964), Kabir (1965), and Kabir (1966) is also cited. The calculations of Wessel and Phillipson (1964), Halpern (1964b), Carter (1965), and Kabir (1966) yielded remarkably consistent results for the overlap and obtained larger binding energies than the adiabatic calculations.

The large amount of effort that has been applied to study of the hydrogen molecular ion demonstrates the importance that is attached to obtaining the best description of its properties. The present investigation was undertaken to provide an independent estimate of the overlap γ by a method different from that of the variational calculations. The present method uses the exact electronic energies and wave functions of Bates, Ledsham, and Stewart (1953) to effect the coupling scheme proposed by Cohen, Judd, and Riddell (1960a). In the present work coupling terms, which

constitute corrections to the adiabatic approximation, are calculated for the homonuclear case. Convergence of certain physical quantities is studied as the basis is increased from one electronic state to six. The physical quantities include the overlap, the energy, the internuclear separation, and the square of the internuclear separation. Behavior of these quantities is also examined as the mass ratio $\epsilon = 4m_\mu / (2m_p + m_\mu)$ is varied from 0.213 for $(p\mu p)^+$ to $1.09 \cdot 10^{-3}$ for $(pep)^+$. The adiabatic electric quadrupole moment is calculated. As an extension of the method of Cohen, Judd, and Riddell (1960a), the formal coupled equations for the motion are worked out from rotation matrices for a general value of the total orbital angular momentum L ; and two solutions ($L = 0$ and $L = 1$) are calculated numerically for the systems studied.

The resultant value for the overlap of ortho, $L = 1$, $(p\mu p)^+$ is applied to the weak interaction as follows. Primakoff (1959) uses the notation $g_V^{(\mu)}$, $g_A^{(\mu)}$, and $g_p^{(\mu)}$ for the weak interaction coupling constants corresponding to vector, axial vector, and induced pseudoscalar coupling, respectively, in the theory of the universal Fermi interaction (De Benedetti, 1964). He takes the weak magnetism coupling constant $g_M^{(\mu)}$ to be, from analogy to the electromagnetic form factors, the difference of the anomalous magnetic moments of the proton and neutron, $g_M^{(\mu)} / g_V^{(\mu)} = 3.706$, and estimates that $g_V^{(\mu)} = 0.972 g_V^{(\beta)}$, where $g_V^{(\beta)}$ is the vector coupling constant for β -decay. However, reliable determinations of $g_A^{(\mu)}$ and $g_p^{(\mu)}$ from theory have been found to be difficult, because they must be renormalized; and recourse to experiment is

presently essential. A good value of $g_A^{(\mu)}$ is necessary in order to determine $g_p^{(\mu)}$. The axial vector coupling constant $g_A^{(\mu)}$ is expected to have a value close to that for beta decay, $g_A^{(\beta)} = -1.18 g_V^{(\beta)}$: $0.97 < g_A^{(\beta)}/g_V^{(\beta)} < 1$ (Lee and Wu, 1965). Theoretical predictions of the induced pseudoscalar constant $g_p^{(\mu)}$ yield $g_p^{(\mu)}/g_A^{(\mu)} \approx 8$ (Goldberger and Treiman, 1958, and Wolfenstein, 1958) from the single-pion pole contribution. The mu mesic hydrogen molecular ion has long been expected to yield significant information concerning these constants (Primakoff, 1959), because it is free of uncertainties in the nuclear matrix elements for muon capture.

The sequence of events leading to muon capture in hydrogen has been well summarized by Rothberg et al. (1963) and Rubbia (1964). Practically all of the capture events observed by Rothberg et al. (1963) for $(p\mu p)^+$ occur in the ortho ($L = 1$) state with total spin $\frac{1}{2}$ (Halpern, 1964a), and the capture rate is directly dependent on the overlap γ_0 of this system (Primakoff, 1959). Weinberg (1960) obtained a value, $\gamma_0 \approx 0.58 \pi^{-1} a_{p\mu}^{-3}$ (Equation 3.83), using the adiabatic wave functions of Cohen, Judd, and Riddell (1960a). Another value, $\gamma_0 \approx 0.50 \pi^{-1} a_{p\mu}^{-3}$, has been calculated by several authors (Wessel and Phillipson, 1964; Halpern, 1964b; Carter, 1966, and Kabir, 1966), using variational wave functions. The two methods differ by about 16 per cent. At the currently accepted value of $g_A^{(\mu)} / g_V^{(\beta)} = -1.18 \pm 0.02$ (Lee and Wu, 1965), $\gamma_0 \approx 0.58 \pi^{-1} a_{p\mu}^{-3}$ corresponds to $g_p^{(\mu)} / g_A^{(\mu)} \approx 15$ (Rothberg et al., 1963), but $\gamma_0 \approx 0.50 \pi^{-1} a_{p\mu}^{-3}$ corresponds to $g_p^{(\mu)} / g_A^{(\mu)} \approx 9$.

The value $g_p^{(\mu)} / g_A^{(\mu)} \approx 9$ compares favorably with the prediction $g_p^{(\mu)} / g_A^{(\mu)} \approx 8$ of Goldberger and Treiman (1958). Further confirmation of the Goldberger-Treiman value was apparently obtained by calculations of the muon capture rate in He^3 done by Oakes (1964) and Bietti (1965), based on the work of Primakoff (1959) and Fujii and Primakoff (1959). These calculations showed that, although the He^3 capture rate was not very sensitive to the value of $g_p^{(\mu)} / g_A^{(\mu)}$, good agreement with the experimental result of Auerbach et al. (1965) was obtained with the choice of $g_A^{(\mu)} / g_V^{(\beta)} = -1.19$ and $g_p^{(\mu)} / g_A^{(\mu)} = 7$.

The experimental result of Conversi et al. (1964) for radiative capture of muons in Ca^{40} indicated, however, that $g_p^{(\mu)} / g_A^{(\mu)} \approx 13$ at $g_A^{(\mu)} / g_V^{(\beta)} = -1.20$. Fearing (1966) reexamined the experimental result of Conversi et al. (1964), using an improved nuclear model, and obtained $g_p^{(\mu)} / g_A^{(\mu)} \approx 16$ at $g_A^{(\mu)} / g_V^{(\beta)} = -1.18$.

The present work was undertaken to help resolve the quantitative uncertainty in these weak interaction coupling constants. The present method, a generalization of the adiabatic approximation of Cohen, Judd, and Riddell (1960a), yields the value $\lambda_0 = 0.56 \pi^{-1} a_{\mu}^{-3}$ for the overlap. Using the experimental result of Rothberg et al. (1963), one obtains $g_p^{(\mu)} / g_A^{(\mu)} = 13.2 \pm 3.5$ at the currently accepted value of $g_A^{(\mu)} / g_V^{(\beta)} = -1.18$. One notes that the results for muon capture in hydrogen, in He^3 , and in Ca^{40} can simultaneously be fit using $g_p^{(\mu)} / g_A^{(\mu)} = 16.2 \pm 3.2$ with $g_A^{(\mu)} / g_V^{(\beta)} = -1.26 \begin{cases} +0.05 \\ -0.04 \end{cases}$. The latter region includes the values quoted by Lee and Wu (1965), $g_A^{(\beta)} / g_V^{(\beta)} = -(1.25 \pm 0.03)$, that are obtained from the asymmetry of neutrinos from beta decay of neutrons.

CHAPTER II

DERIVATION OF COUPLED EQUATIONS OF MOTION

This derivation is posed in the framework developed by Cohen, Judd, and Riddell (1960a), but it includes a more general treatment of the angular momentum variables. For this reason, the entire development is given below, keeping the notation as similar to that of Cohen, Judd, and Riddell (1960a) as possible. One assumes there is no dynamical effect of spin other than the exchange antisymmetry required of the wave function by the Pauli principle. Schrödinger's equation for the hydrogen molecular ion is

$$\left\{ -\frac{\hbar^2}{2} \left(\frac{\nabla_1^2}{m_1} + \frac{\nabla_2^2}{m_2} + \frac{\nabla_\mu^2}{m_\mu} \right) + V \right\} \psi = E \psi,$$

where the subscripts on the Laplacians denote differentiation with respect to the appropriate particle variables. Particles 1 and 2 refer to hydrogen nuclei, and particle μ denotes either a muon or an electron. Particle μ is assumed to be a muon in the following. The potential V is taken to be

$$V = -\frac{e^2}{|\vec{r}_\mu - \vec{r}_1|} - \frac{e^2}{|\vec{r}_\mu - \vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}.$$

This potential neglects any nuclear forces which may enter at very small separations.

I. TRANSFORMATION TO CENTER OF MASS AND RELATIVE COORDINATES

Observing that the potential is a function only of relative coordinates, one first effects a transformation to center of mass and relative coordinates:

the center of mass is defined by

$$M_t \vec{r}_c = m_1 \vec{r}_1 + m_2 \vec{r}_2 + m_\mu \vec{r}_\mu ,$$

the internuclear separation by

$$\vec{r}_n = \vec{r}_1 - \vec{r}_2 ,$$

and the muon coordinates by

$$\vec{R}_\mu = \vec{r}_\mu - f_1 \vec{r}_1 - f_2 \vec{r}_2 ,$$

where

$$M_t = m_1 + m_2 + m_\mu , \quad (2.1)$$

$$f_1 = \frac{m_1}{m_1 + m_2} , \quad f_2 = \frac{m_2}{m_1 + m_2} , \text{ and } f_1 + f_2 = 1 . \quad (2.2)$$

Then the sum of the mass-weighted Laplacians becomes

$$\begin{aligned} & \frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 + \frac{1}{m_\mu} \nabla_\mu^2 \\ &= \frac{1}{M_t} \nabla_c^2 + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_n^2 + \left(\frac{f_1^2}{m_1} + \frac{f_2^2}{m_2} + \frac{1}{m_\mu} \right) \nabla_\mu^2 , \end{aligned}$$

where $(f_1^2/m_1 + f_2^2/m_2) = 1/(m_1 + m_2)$.

Let

$$\frac{1}{M_n} = \frac{1}{m_1} + \frac{1}{m_2}, \text{ such that } M_n = \frac{m_1 m_2}{m_1 + m_2}, \quad (2.3)$$

$$\text{and } \frac{1}{M_\mu} = \frac{f_1^2}{m_1} + \frac{f_2^2}{m_2} + \frac{1}{m_\mu} = \frac{1}{m_1 + m_2} + \frac{1}{m_\mu},$$

$$\text{such that } M_\mu = \frac{m_\mu (m_1 + m_2)}{M_t}. \quad (2.4)$$

One thus has the following form for Schrödinger's equation:

$$\left\{ -\frac{\hbar^2}{2} \left(\frac{1}{M_t} \nabla_c^2 + \frac{1}{M_n} \nabla_n^2 + \frac{1}{M_\mu} \nabla_\mu^2 \right) + \frac{e^2}{r_n} - \frac{e^2}{r_{\mu 1}} - \frac{e^2}{r_{\mu 2}} \right\} \psi' = E' \psi'.$$

The uniform motion of the center of mass is removed by the substitution

$$\psi' = \exp(i \vec{P}_c \cdot \vec{r}_c / \hbar) \psi(\vec{r}_n', \vec{R}_\mu'), \text{ where } \vec{P}_c \text{ is a constant vector.}$$

The center of mass of the system may now be regarded as stationary in a laboratory system. Introducing the reduced Bohr radius $a_\mu = \hbar^2 / (M_\mu e^2)$ as the unit of length such that $\vec{r}_n = \vec{r}_n' / a_\mu$ and $\vec{R}_\mu = \vec{R}_\mu' / a_\mu$, and the Rydberg

$$W_\mu = e^4 M_\mu / (2 \hbar^2) = \frac{M_\mu c^2 \alpha^2}{2} \text{ as the unit of energy, such that } E = E' / W_\mu, \text{ the}$$

Schrödinger equation becomes

$$\left\{ -\frac{\hbar^2}{2} \left(\frac{1}{M_n} \cdot \frac{1}{a_\mu^2} \nabla_n^2 + \frac{1}{M_\mu} \cdot \frac{1}{a_\mu^2} \nabla_\mu^2 \right) + \frac{e^2}{a_\mu r_n} - \frac{e^2}{a_\mu r_{\mu 1}} - \frac{e^2}{a_\mu r_{\mu 2}} \right\} \psi = W_\mu \cdot E \psi$$

or

$$\left\{ -\left(\frac{\hbar^2}{2M_n} \cdot \frac{1}{a_\mu^2 W_\mu} \nabla_n^2 + \frac{\hbar^2}{2M_\mu} \cdot \frac{1}{a_\mu^2 W_\mu} \nabla_\mu^2 \right) + \frac{e^2}{a_\mu W_\mu} \left(\frac{1}{r_n} - \frac{1}{r_{\mu 1}} - \frac{1}{r_{\mu 2}} \right) \right\} \psi = E \psi$$

Since

$$\frac{\hbar^2}{2M_n} \cdot \frac{1}{a_\mu^2 W_\mu} = \left(\frac{\hbar^2}{2M_n} \right) \cdot \left(\frac{M_\mu e^2}{\hbar^2} \right)^2 \cdot \left(\frac{2\hbar^2}{M_\mu e^4} \right) = \frac{M_\mu}{M_n},$$

$$\frac{\hbar^2}{2M_\mu} \cdot \frac{1}{a_\mu^2 W_\mu} = 1,$$

and

$$\frac{e^2}{a_\mu W_\mu} = (e^2) \cdot \left(\frac{M_\mu e^2}{\hbar^2} \right) \cdot \left(\frac{2\hbar^2}{M_\mu e^4} \right) = 2,$$

one obtains as the dimensionless Schrödinger equation

$$\left\{ -\epsilon \nabla_n^2 - \nabla_\mu^2 + \frac{2}{r_n} - \frac{2}{r_{\mu 1}} - \frac{2}{r_{\mu 2}} \right\} \psi = E \psi, \quad (2.5)$$

where $\epsilon = \frac{M_\mu}{M_n} = \frac{4m_\mu}{2m_p + m_\mu}$. This equation was obtained by Cohen, Judd,

and Riddell (1960a), who limited their discussion of the solutions to the lowest rotational level. In the following sections, more general results are obtained for the coupling parameters and the solutions in the homonuclear case.

II. ANGULAR DEPENDENCE OF THE TOTAL SPATIAL WAVE FUNCTION

It is convenient to first extract the angular dependence of the total spatial wave function $\psi(\vec{r}_n, \vec{R}_\mu)$. Let a given solution be labeled by its total orbital angular momentum $\vec{L}$ and by M , the projection of $\vec{L}$ in the laboratory $\hat{z}_L$ - direction. Considering the coordinate system of Figure 1, page 13, one defines

$$\psi_M^L(\phi_n = 0, \theta_n = 0, \phi = 0; r_n, \xi, \eta) \equiv G_M^L(r_n, \xi, \eta),$$

in which the Euler angles are

ϕ_n = azimuthal angle of the body-fixed axis $\hat{x}_n$ in the laboratory system,

θ_n = polar angle of the internuclear axis, $\hat{r}_n = \hat{z}_n$, in the laboratory system, and

ϕ = azimuthal angle of the muon in the body-fixed coordinate system,

and the other variables are the internuclear separation r_n ,

$$\xi = (r_{\mu 1} + r_{\mu 2})/r_n \text{ and } \eta = (r_{\mu 1} - r_{\mu 2})/r_n.$$

Note that ϕ_n is the first rotation of the coordinate system, θ_n the second, and ϕ the third.

The wave function at an arbitrary point of configuration space is (Wigner, 1959)

$$\psi_M^L(\phi_n, \theta_n, \phi; r_n, \xi, \eta) = \sum_{K=-L}^L D_{MK}^{L*}(\Pi - \phi_n, \theta_n, -\Pi - \phi)$$

$$\cdot G_K^L(r_n, \xi, \eta),$$

FIGURE 1

ORIENTATION OF THE BODY-FIXED COORDINATE SYSTEM RELATIVE
TO THE LABORATORY SYSTEM, SHOWING THE
EULER ANGLES ϕ_n , θ_n , AND ϕ

where the projection of $\vec{L}$ on the internuclear axis is K . From the definition

$$D_{MK}^{L*}(\alpha, \beta, \gamma) = e^{-iM\alpha} d_{MK}^L(\beta) e^{-iK\gamma},$$

in which $d_{MK}^L(\beta)$ is real, one obtains

$$\begin{aligned} D_{MK}^{L*}(\Pi - \phi_n, \theta_n, -\Pi - \phi) &= e^{-i\Pi(M-K)} e^{+iM\phi_n} d_{MK}^L(\theta_n) e^{iK\phi} \\ &= (-)^{M-K} D_{MK}^L(\phi_n, \theta_n, \phi). \end{aligned}$$

Thus, the total spatial wave function becomes

$$\psi_M^L(\phi_n, \theta_n, \phi; r_n, \xi, \eta) = \sum_{K=-L}^L (-)^{M-K} D_{MK}^L(\phi_n, \theta_n, \phi) G_K^L(r_n, \xi, \eta). \quad (2.7)$$

III. PARITY OF THE TOTAL SPATIAL WAVE FUNCTION

The parity of the total spatial wave function is determined by the spatial inversion (even-odd) symmetry and may be established by the following reasoning: if the positions of the three particles are inverted in the center of mass, the Euler angles become $\{\phi_n + \Pi, \Pi - \theta_n, \Pi - \phi\}$, see Figure 1, page 13. Therefore, if P_I is the inversion operator,

$$\begin{aligned} P_I \{ \psi_M^L(\phi_n, \theta_n, \phi; r_n, \xi, \eta) \} &= \sum_K (-)^{M-K} D_{MK}^L(\phi_n + \Pi, \Pi - \theta_n, \Pi - \phi) \\ &\cdot G_K^L(r_n, \xi, \eta). \end{aligned}$$

From

$$d_{MK}^L(\Pi - \theta_n) = (-)^{L-M} d_{M, -K}^L(\theta_n) \quad (\text{Wigner, 1959}),$$

one has

$$\begin{aligned}
 P_I \{ \psi_M^L(\phi_n, \theta_n, \phi; r_n, \xi, \eta) \} &= \sum_K (-)^{M-K} [(-)^{L-M} e^{iM(\phi_n + \Pi)} d_{M, -K}^L(\theta_n) \\
 &\quad \cdot e^{iK(\Pi - \phi)}] G_K^L(r_n, \xi, \eta) \\
 &= \sum_K (-)^{M-K} e^{iM\phi_n} d_{M, -K}^L(\theta_n) e^{-iK\phi} \cdot [(-)^{L+K} G_K^L(r_n, \xi, \eta)] \\
 &= \sum_K (-)^{M-K} D_{M, -K}^L(\phi_n, \theta_n, \phi) \cdot [(-)^{L+K} G_K^L(r_n, \xi, \eta)] \\
 &= \sum_K (-)^{M+K} D_{M, K}^L(\phi_n, \theta_n, \phi) \cdot [(-)^{L-K} G_{-K}^L(r_n, \xi, \eta)] \\
 &= \sum_K (-)^{M-K} D_{M, K}^L(\phi_n, \theta_n, \phi) \cdot [(-)^{L-K} G_{-K}^L(r_n, \xi, \eta)] \quad (2.8)
 \end{aligned}$$

The result of this operation must be $\pm \psi_L^M(\phi_n, \theta_n, \phi; r_n, \xi, \eta)$:

$$P_I \psi_L^M(\phi_n, \theta_n, \phi; r_n, \xi, \eta) = \Pi_I \psi_L^M(\phi_n, \theta_n, \phi; r_n, \xi, \eta);$$

where $\Pi_I = +$ corresponds to a function having even parity, or $\Pi_I = -$ corresponds to a function having odd parity.

Let the parity Π_I of the total spatial wave function be denoted by + or - superscripts on the total spatial wave function, as in

$$\pm \psi_M^L(\phi_n, \theta_n, \phi; r_n, \xi, \eta) = \sum_{K=-L}^L (-)^{M-K} D_{MK}^L(\phi_n, \theta_n, \phi) G_K^{L, \pm}(r_n, \xi, \eta).$$

Note that the function $G_K^{L,+}(r_n, \xi, \eta)$ is always even under spatial inversion but that it has here been labeled to correspond to the overall parity of the total spatial function. Further (dropping the arguments),

$$P_I \psi_M^L = \pm \psi_M^L .$$

Thus

$$G_K^{L,+} = \pm (-)^{L-K} G_{-K}^{L,+} \quad (2.9)$$

or

$$G_{-K}^{L,+} = \pm (-)^{L+K} G_K^{L,+} . \quad (2.10)$$

One notes that, for $K = 0$,

$$G_0^{L,+} = \pm (-)^L G_0^{L,+} ;$$

thus, for even values of L , one has

$$G_0^{L,+} = + G_0^{L,+} , \quad L \text{ even} .$$

From this result one has explicitly

$$G_0^{L,+} = + G_0^{L,+} , \quad L \text{ even}, \quad (2.11)$$

and

$$G_0^{L,-} = - G_0^{L,-} , \quad L \text{ even}. \quad (2.12)$$

The only function which can satisfy the latter relationship is

$$G_0^{L,-} = 0, \quad L \text{ even.} \quad (2.13)$$

For odd values of L , one obtains

$$G_0^{L,+} = - G_0^{L,-}, \quad L \text{ odd,}$$

from which

$$G_0^{L,+} = - G_0^{L,+}, \quad L \text{ odd} \quad (2.14)$$

and

$$G_0^{L,-} = + G_0^{L,-}, \quad L \text{ odd.} \quad (2.15)$$

The even parity function in the case of odd L can only be

$$G_0^{L,+} = 0, \quad L \text{ odd.} \quad (2.16)$$

One can thus express the total spatial wave function in general as

$$\begin{aligned} \psi_M^L(\phi_n, \theta_n, \phi; r_n, \xi, \eta) = & (-)^M D_{M0}^L(\phi_n, \theta_n, \phi) \cdot [G_0^{L,+}(r_n, \xi, \eta) \cdot \delta_{L, \text{even}} \delta_{\Pi_I}, \\ & + G_0^{L,-}(r_n, \xi, \eta) \cdot \delta_{L, \text{odd}} \delta_{\Pi_I}^-] \\ & + \sum_{K>0}^L (-)^{M-K} [D_{MK}^L(\phi_n, \theta_n, \phi) \pm (-)^{L+K} D_{M,-K}^L(\phi_n, \theta_n, \phi)] G_K^{L,\pm}(r_n, \xi, \eta). \end{aligned}$$

It is sufficient to choose any one value of M to effect a solution. Let $M = 0$ for simplicity, and drop the arguments on the right hand side in the above equation:

$$\begin{aligned}
& {}^{\pm} \psi_O^L (\phi_n, \theta_n, \phi; r_n, \xi, \eta) \\
& = D_{OO}^L \cdot [G_O^{L,+} \cdot \delta_{L,\text{even}} \delta_{\Pi_I,+} + G_O^{L,-} \cdot \delta_{L,\text{odd}} \delta_{\Pi_I,-}] \\
& + \sum_{K>0}^L (-)^K [D_{OK}^L \pm (-)^{L+K} D_{0,-K}^L] \cdot G_K^{L,\pm} . \quad (2.17)
\end{aligned}$$

One has (Wigner, 1959)

$$\begin{aligned}
D_{OK}^L (\phi_n, \theta_n, \phi) &= \sqrt{\frac{4\pi}{2L+1}} Y_{LK} (\theta_n, \phi) , \\
D_{0,-K}^L (\phi_n, \theta_n, \phi) &= (-)^K \sqrt{\frac{4\pi}{2L+1}} Y_{LK}^* (\theta_n, \phi) ,
\end{aligned}$$

and

$$D_{0,0}^L (\phi_n, \theta_n, \phi) = P_L (\cos \theta_n) ,$$

where $Y_{LK} (\theta_n, \phi)$ is a spherical harmonic,

$$Y_{LK} (\theta_n, \phi) = (-)^K \sqrt{\frac{(2L+1)}{4\pi} \cdot \frac{(L-K)!}{(L+K)!}} P_L^K (\cos \theta_n) e^{iK\phi} ,$$

and

$$P_L^K (\cos \theta_n) \text{ is an associated Legendre function.}$$

Thus,

$$\begin{aligned}
[D_{OK}^L \pm (-)^{L+K} D_{0,-K}^L] &= \sqrt{\frac{4\pi}{2L+1}} \cdot [Y_{LK} (\theta_n, \phi) \pm (-)^L Y_{LK}^* (\theta_n, \phi)] \\
&= \sqrt{\frac{4\pi}{2L+1}} \cdot (-)^K \sqrt{\frac{(2L+1)}{4\pi} \cdot \frac{(L-K)!}{(L+K)!}} P_L^K (\cos \theta_n) \cdot [e^{iK\phi} \pm (-)^L e^{-iK\phi}]
\end{aligned}$$

$$\begin{aligned}
&= (-)^K \cdot 2 \cdot \sqrt{\frac{(L-K)!}{(L+K)!}} \cdot P_L^K(\cos \theta_n) \cdot [\delta_{L,\text{even}} \cdot (\delta_{\Pi_I,+} \cos K\phi + i \delta_{\Pi_I,-} \sin K\phi) \\
&\quad + \delta_{L,\text{odd}} \cdot (\delta_{\Pi_I,-} \cos K\phi + i \delta_{\Pi_I,+} \sin K\phi)] \\
&= (-)^K \cdot 2 \cdot \sqrt{\frac{(L-K)!}{(L+K)!}} \cdot P_L^K(\cos \theta_n) \cdot [(\delta_{L,\text{even}} \delta_{\Pi_I,+} + \delta_{L,\text{odd}} \delta_{\Pi_I,-}) \cos K\phi \\
&\quad + i(\delta_{L,\text{even}} \delta_{\Pi_I,-} + \delta_{L,\text{odd}} \delta_{\Pi_I,+}) \sin K\phi] .
\end{aligned}$$

From the above results, the $M = 0$ function is independent of ϕ_n , and Equation (2.17) becomes

$$\begin{aligned}
\Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) &= \sum_{K=0}^L A_{LK} P_L^K(\cos \theta_n) G_K^{L, \Pi_I}(r_n, \xi, \eta) \\
&\quad \cdot [(\delta_{L,\text{even}} \delta_{\Pi_I,+} + \delta_{L,\text{odd}} \delta_{\Pi_I,-}) \cdot \cos K\phi \\
&\quad + i(\delta_{L,\text{even}} \delta_{\Pi_I,-} + \delta_{L,\text{odd}} \delta_{\Pi_I,+}) \sin K\phi] , \tag{2.18}
\end{aligned}$$

where

$$A_{LK} = (2 - \delta_{K,0}) \sqrt{\frac{(L-K)!}{(L+K)!}} \tag{2.19}$$

and the term for $K = 0$ in the sum automatically vanishes if L is even and Π_I is minus or if L is odd and Π_I is plus.

In particular, one has, for $L = \text{even}$ and $\Pi_I = +$ or $L = \text{odd}$ and $\Pi_I = -$,

$$\Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = \sum_{K=0}^L A_{LK} P_L^K(\cos \theta_n) G_K^{L, \Pi_I}(r_n, \xi, \eta) \cos K\phi \quad (2.20)$$

One also obtains, for $L = \text{even}$ and $\Pi_I = -$ or $L = \text{odd}$ and $\Pi_I = +$,

$$\Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = \sum_{K=1}^L A_{LK} P_L^K(\cos \theta_n) G_K^{L, \Pi_I}(r_n, \xi, \eta) \sin K\phi, \quad (2.21)$$

in which $i = \sqrt{-1}$ has been dropped.

IV. GERADE-UNGERADE SYMMETRY

If the two nuclei have the same charge, the three-body system has an additional symmetry, which will be called the gerade-ungerade symmetry. The total spatial wave function must be symmetric (gerade) or antisymmetric (ungerade) to inversion of the muon (or electron) in the center of the inter-nuclear axis, keeping the two nuclei fixed (Herzberg, 1957). Referring to Equation (2.26) below, one takes $\xi = (r_{\mu 1} + r_{\mu 2})/r_n$, $\eta = (r_{\mu 1} - r_{\mu 2})/r_n$, and ϕ as the muon coordinates in the body-fixed coordinate system. Referring to Figure 1, page 13, the coordinates change as follows in inversion of the muon:

$$\phi_n \rightarrow \phi_n,$$

$$\theta_n \rightarrow \theta_n,$$

$$\phi \rightarrow \phi \pm \Pi,$$

$$r_n \rightarrow r_n,$$

$$\xi \rightarrow \xi,$$

and

$$\eta \rightarrow -\eta.$$

Letting P_μ denote inversion of the muon, one has

$$P_\mu \{ {}^{\Pi_I} \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) \} = {}^{\Pi_I} \psi_0^L(\theta_n, \phi \pm \Pi; r_n, \xi, -\eta).$$

In turn,

$${}^{\Pi_I} \psi_0^L(\theta_n, \phi \pm \Pi; r_n, \xi, -\eta) = \Pi_\mu {}^{\Pi_I} \psi_0^L(\theta_n, \phi; r_n, \xi, \eta),$$

where the gerade-ungerade symmetry is Π_μ :

$$\Pi_\mu = +1 \text{ is referred to as gerade (g)}$$

and

$$\Pi_\mu = -1 \text{ is referred to as ungerade (u).}$$

In the following, the total spatial wave function is labeled by its gerade-ungerade symmetry Π_μ : ${}^{\Pi_\mu, \Pi_I} \psi_0^L(\theta_n, \phi; r_n, \xi, \eta)$. One notes that

$$\cos K(\phi \pm \Pi) = (-)^K \cos K\phi$$

and

$$\sin K(\phi \pm \Pi) = (-)^K \sin K\phi;$$

from the above one has

$$P_{\mu} \begin{Bmatrix} \cos K\phi \\ \sin K\phi \end{Bmatrix} = (-)^K \begin{Bmatrix} \cos K\phi \\ \sin K\phi \end{Bmatrix}.$$

Let the factor $G_K^{L, \Pi_I, \Pi_{\mu}}(r_n, \xi, \eta)$ be labeled by the gerade-ungerade symmetry Π_{μ} of the total spatial wave function $\Pi_{\mu}, \Pi_I \psi_0^L$.

One has

$$\begin{aligned} \Pi_{\mu} G_K^{L, \Pi_I, \Pi_{\mu}}(r_n, \xi, \eta) \\ = (-)^K P_{\mu} \{ G_K^{L, \Pi_I, \Pi_{\mu}}(r_n, \xi, \eta) \} = (-)^K G_K^{L, \Pi_I, \Pi_{\mu}}(r_n, \xi, -\eta). \end{aligned} \quad (2.22)$$

Thus, the gerade-ungerade symmetry of the factor $G_K^{L, \Pi_I, \Pi_{\mu}}$ is the same as that of the total spatial wave function for even values of K and is opposite that of the total spatial wave function for odd values of K :

$$G_K^{L, \Pi_I, \Pi_{\mu}}(r_n, \xi, -\eta) = \Pi_{\mu} \cdot (-)^K G_K^{L, \Pi_I, \Pi_{\mu}}(r_n, \xi, \eta). \quad (2.23)$$

V. EXCHANGE SYMMETRY IN THE HOMONUCLEAR CASE

If the two nuclei are identical (the homonuclear or equal-mass case), the exchange symmetry of the total wave function, including space and spin variables, under inversion of two nuclei must be taken into account. Let the exchange operation be called P_E . It has the following effect on the space variables: the two nuclei are inverted in the midpoint of the inter-nuclear axis, keeping the muon fixed in space. Thus, particle 1 becomes particle 2, particle 2 becomes particle 1, and the angular coordinates are changed because the vector $\vec{r}_n$ takes the opposite direction in physical

space. Under P_E one has from Figure 1, page 13,

$$\phi_n \rightarrow \phi_n \pm \Pi,$$

$$\theta_n \rightarrow \Pi - \theta_n,$$

$$\phi \rightarrow -\phi, 2\Pi - \phi,$$

$$r_n \rightarrow r_n,$$

$$\xi \rightarrow \xi,$$

and

$$\eta \rightarrow -\eta.$$

The operation denoted by P_E is seen to be spatially equivalent to two successive operations, inversion in the center of mass of all of the particles (P_I) followed by inversion of the muon in the center of the internuclear axis (P_μ):

$$P_E = P_\mu P_I.$$

This equivalence is demonstrated below:

$$\phi_n \xrightarrow{P_I} \phi_n \pm \Pi \xrightarrow{P_\mu} \phi_n \pm \Pi,$$

$$\theta_n \xrightarrow{P_I} \Pi - \theta_n \xrightarrow{P_\mu} \Pi - \theta_n,$$

$$\phi \xrightarrow{P_I} \Pi - \phi \xrightarrow{P_\mu} -\phi, 2\Pi - \phi,$$

$$r_n \xrightarrow{P_I} r_n \xrightarrow{P_\mu} r_n,$$

$$\begin{matrix} P_I & P_\mu \\ \xi \rightarrow & \xi \rightarrow \xi \end{matrix},$$

and

$$\begin{matrix} P_I & P_\mu \\ \eta \rightarrow & \eta \rightarrow -\eta \end{matrix}.$$

Thus, the effect of the operator P_E on the total spatial wave function is the product of the effects of P_I and P_μ , and one obtains

$$P_E^{\pi_\mu, \pi_I} \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = \pi_E^{\pi_\mu, \pi_I} \psi_0^L(\theta_n, \phi; r_n, \xi, \eta),$$

where

$$\pi_E = \pi_\mu \pi_I. \quad (2.24)$$

Consequently, the spatial exchange symmetry of the nuclei is antisymmetric ($\pi_E = -1$) if $\pi_\mu = g$ and $\pi_I = -$ or if $\pi_\mu = u$ and $\pi_I = +$. The spatial exchange symmetry of the nuclei is symmetric ($\pi_E = +1$) if $\pi_\mu = g$ and $\pi_I = +$ or if $\pi_\mu = u$ and $\pi_I = -$.

It is noted that the symmetry of Σ -states of diatomic molecules to reflection of the leptons in a plane containing the internuclear axis is plus, if there is only one lepton. This symmetry will not be further considered in the following work.

Finally, one notes that, if the two identical nuclei in the homonuclear case are fermions, a symmetric total spatial wave function ($\pi_E = +1$) is associated with a spin state which is antisymmetric in the nuclei, as in the "para" state of the system $(pup)^+$, $S_{pp} = 0$. On the other hand, if the nuclei are bosons, a $\pi_E = +1$ total spatial wave function is associated with a symmetric spin state, as in $S_{dd} = 0$ or 2 for $(dud)^+$. For an antisymmetric total spatial wave function ($\pi_E = -1$), the spin state of the nuclei is symmetric for fermions (the "ortho" state for pup , $S_{pp} = 1$) and antisymmetric for bosons.

VI. ELECTRONIC WAVE FUNCTIONS AND ELECTRONIC ENERGIES

In following sections the total spatial wave function shall be expanded in the clamped-nuclei wave functions derived by Bates, Ledsham, and Stewart (1953) for the hydrogen molecular ion (H_2^+). These functions are sometimes called "two-center" wave functions. The clamped-nuclei functions shall be here referred to as the electronic states, regardless of whether a muon or an electron is the orbiting particle. Similarly, the eigenenergies associated with the clamped nuclei eigenfunctions shall be called electronic energies. The normalization of the electronic states used in the present work is different from that of Bates, Ledsham, and Stewart (1953). In order to present the explicit form, the electronic wave functions are briefly developed below. The orbiting particle is assumed to be a muon.

The electronic states will be symbolized by the subscript or superscript i denoting the united atom ($r_n = 0$) convention of Bates, Ledsham, and Stewart (1953):

$$|i\rangle \rightarrow |n_i \ell_i m_{i\mu}\rangle ,$$

where n_i is the principal quantum number of the united atom, ℓ_i is the orbital quantum number, and m_i is the magnetic quantum number. The united atom states are designated by Bates, Ledsham, and Stewart (1953) by four symbols: (1) the number n_i ; (2) a letter s, p, d, f, g, ...etc., corresponding, respectively, to the values $\ell_i = 0, 1, 2, 3, 4, \dots$ etc.; (3) a

Greek symbol σ , Π , ... etc., corresponding, respectively, to the values $|m_i| = 0, 1, \dots$ etc.; and (4) a subscript g for gerade or u for ungerade (the gerade-ungerade symmetry of the electronic state is determined uniquely by (2) above, see Equation 2.49). Thus, the lowest electronic state is called $1s\sigma_g$.

The same states called "united atom" states by Bates, Ledsham, and Stewart (1953) are called the "molecule" states by Kotani, Ohno, and Kayama (1961). The latter authors note that

United Atom	Molecule	Separated Atoms
$n_r = n_i - \ell_i - 1 \rightarrow n_\xi \rightarrow$		n_λ ,
$n_s = \ell_i - m_i \rightarrow n_\eta \rightarrow$		$\begin{cases} 2n_\mu, n_\eta = \text{even} \\ 2n_\mu + 1, n_\eta = \text{odd} \end{cases}$
and $n_\phi = m_i \rightarrow n_\phi \rightarrow$		n_ϕ ,

where n_λ , n_μ , and n_ϕ are the n_r , n_θ , and n_ϕ values, respectively, for the separated atoms ($r_n \rightarrow \infty$). Table I, page 27, presents the quantum numbers for the electronic states used in following sections as basis functions.

Assuming the nuclei to be fixed at a given internuclear separation $\vec{r}_n$, Schrödinger's equation simplifies to

$$H_\mu \psi_i(\vec{R}_\mu, \vec{r}_n) = W_i(r_n) \cdot \psi_i(\vec{R}_\mu, \vec{r}_n) ;$$

where the mesic Hamiltonian is

$$H_\mu = -\frac{\hbar^2}{2M_\mu} \nabla_\mu^2 - \frac{e^2}{r_{\mu 1}} - \frac{e^2}{r_{\mu 2}} ,$$

i labels the electronic state, such as $1s\sigma_g$, and $M_\mu = \frac{m_\mu(m_1+m_2)}{m_1+m_2+m_\mu}$. Choosing

TABLE I

UNITED ATOM AND SEPARATED ATOM QUANTUM NUMBERS OF ELECTRONIC STATES USED AS BASIS FUNCTIONS

United Atom Symbol i	United Atom			Molecule			Separated Atoms			Separated Atoms Symbol
	n_i	ℓ_i	m_i	n_ξ	n_η	n_ϕ	n_λ	n_μ	n_ϕ	
$1s\sigma_g$	1	0	0	0	0	0	0	0	0	1s
$2s\sigma_g$	2	0	0	1	0	0	1	0	0	2s
$3s\sigma_g$	3	0	0	2	0	0	2	0	0	3s
$3d\sigma_g$	3	2	0	0	2	0	0	1	0	2p(σ)
$3d\pi_g$	3	2	1	0	1	1	0	0	1	2p(π)
$4s\sigma_g$	4	0	0	3	0	0	3	0	0	4s
$4d\sigma_g$	4	2	0	1	2	0	1	1	0	3p(σ)
$4d\pi_g$	4	2	1	1	1	1	1	0	1	3p(π)

to measure distance in units of the Bohr radius $a_\mu = \frac{\hbar^2}{M_\mu e^2}$ and energy in

units of the mesonic Rydberg $W_\mu = \frac{M_\mu e^4}{2\hbar^2} = \frac{M_\mu c^2}{2} \cdot \alpha^2$, where the fine struc-

ture constant $\alpha = \frac{e^2}{\hbar c}$, one has

$$H_\mu \psi_i(\vec{R}_\mu, \vec{r}_n) = W_i(r_n) \cdot \psi_i(\vec{R}_\mu, \vec{r}_n), \quad (2.25)$$

where

$$H_\mu = -\nabla_\mu^2 - \frac{2}{r_{\mu 1}} - \frac{2}{r_{\mu 2}},$$

$$\vec{r}_n = \frac{\vec{r}_n}{a_\mu},$$

$$\vec{R}_\mu = \frac{\vec{R}_\mu}{a_\mu},$$

$$r_{\mu 1} = \frac{r_{\mu 1}}{a_\mu},$$

$$r_{\mu 2} = \frac{r_{\mu 2}}{a_\mu},$$

$$W_i(r_n) = \frac{W_i(r_n)}{W_\mu},$$

and

$$\nabla_\mu^2 = a_\mu^2 \cdot \nabla_\mu'^2.$$

The Laplacian can be expressed in prolate spheroidal (confocal elliptical) coordinates (Lowen, 1965) as

$$\nabla_{\mu}^2 = \frac{4}{r_n^2 \cdot (\xi^2 - \eta^2)} \cdot \left\{ \frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] + \frac{(\xi^2 - \eta^2)}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \phi^2} \right\},$$

where

$$\xi = \frac{r_{\mu 1} + r_{\mu 2}}{r_n}, \quad 1 \leq \xi < \infty, \quad (2.26)$$

$$\eta = \frac{r_{\mu 1} - r_{\mu 2}}{r_n}, \quad -1 \leq \eta \leq 1,$$

and

$$0 \leq \phi \leq 2\pi.$$

The volume element is $d^3R_{\mu} = \frac{r_n^3 (\xi^2 - \eta^2)}{8} d\xi d\eta d\phi$. Following Bates, Ledsham, and Stewart (1953) one lets the electronic wave function be

$$\psi_i(\vec{R}_{\mu}, \vec{r}_n) = \mathcal{N}_i(r_n) \cdot \Lambda_i(\xi, r_n) \cdot M_i(\eta, r_n) \cdot \mathcal{P}_{m_i}(\phi), \quad (2.27)$$

where the normalization has been chosen in the present work to be

$$\int_{R_{\mu}} d^3R_{\mu} |\psi_i(\vec{R}_{\mu}, \vec{r}_n)|^2 = 1 \quad (2.28)$$

with

$$\int_{-1}^1 d\eta |M_i(\eta, r_n)|^2 = 1, \quad (2.29)$$

$$\int_1^{\infty} d\xi |\Lambda_i(\xi, r_n)|^2 = 1, \quad (2.30)$$

$$\int_0^{2\pi} d\phi |\rho_{m_i}(\phi)|^2 = 2\pi, \quad (2.31)$$

and the normalization constant is

$$N_i(r_n) = \frac{4}{\pi r_n^3 \left\{ \int_1^{\infty} d\xi \xi^2 |\Lambda_i(\xi, r_n)|^2 - \int_{-1}^1 d\eta \eta^2 |M_i(\eta, r_n)|^2 \right\}}.$$

This separation of variables leads to the equations

$$\frac{d^2 \rho_{m_i}(\phi)}{d\phi^2} + m_i^2 \rho_{m_i}(\phi) = 0, \quad (2.32)$$

$$\begin{aligned} \frac{d}{d\eta} \left\{ (1-\eta^2) \frac{dM_i(\eta, r_n)}{d\eta} \right\} + \left\{ -A_i(r_n) + [p_i(r_n)]^2 \cdot \eta^2 \right. \\ \left. - \frac{m_i^2}{1-\eta^2} \right\} M_i(\eta, r_n) = 0, \end{aligned} \quad (2.33)$$

and

$$\begin{aligned} \frac{d}{d\xi} \left\{ (\xi^2-1) \frac{d\Lambda_i(\xi, r_n)}{d\xi} \right\} + \left\{ A_i(r_n) + 2r_n \xi \right. \\ \left. - [p_i(r_n)]^2 \cdot \xi^2 - \frac{m_i^2}{\xi^2-1} \right\} \Lambda_i(\xi, r_n) = 0, \end{aligned} \quad (2.24)$$

where

$$[p_i(r_n)]^2 = -\frac{r_n^2}{4} \cdot W_i(r_n). \quad (2.25)$$

One obtains as the solution for the azimuthal dependence

$$\rho_{m_i}^{\tau_\phi}(\phi) = \begin{cases} 1, & m_i = 0, \\ \text{or} \begin{cases} \sqrt{2} \cos m_i \phi \\ \sqrt{2} \sin m_i \phi \end{cases}, & m_i \neq 0, \end{cases}$$

$$= [\delta_{m_i, 0} + \sqrt{2}(1 - \delta_{m_i, 0})] \cdot [\delta_{\tau_\phi, c} \cos m_i \phi + \delta_{\tau_\phi, s} \sin m_i \phi], \quad (2.26)$$

where $\tau_\phi = c$ implies cosine dependence and $\tau_\phi = s$ implies sine dependence.

From Stratton et al. (1941) the "inner" function is

$$M_i(n, r_n) = \sum_{n=0, 1}^{\infty} f_n^{(i)}(r_n) P_{m_i+n}^{m_i}(n), \quad (2.37)$$

where $\sum_{n=0, 1}^{\infty}$ implies a sum over either the even integers from 0 to ∞ or

over the odd integers from 1 to ∞ , $f_n^{(i)}(r_n)$ are expansion coefficients, and $P_{m+n}^m(n)$ are the associated Legendre functions. From Bates, Ledsham, and Stewart (1953) the "outer" function is

$$\Lambda_i(\xi, r_n) = (\xi^2 - 1)^{\frac{m_i}{2}} \cdot (\xi + 1)^{\sigma_i(r_n)} \cdot e^{-p_i(r_n) \cdot \xi} \cdot y_i(\zeta, r_n), \quad (2.38)$$

where

$$\zeta = \frac{\xi - 1}{\xi + 1}, \quad \sigma_i(r_n) = \frac{r_n}{p_i(r_n)} - m_i - 1,$$

and

$$y_i(\zeta, r_n) = \sum_{t=0}^{\infty} g_t^{(i)}(r_n) \cdot \zeta^t, \quad (2.39)$$

in which $g_t^{(i)}(r_n)$ are expansion coefficients. The numerical solution of these equations is treated in more detail on page 83.

VII. EXPANSION OF THE TOTAL SPATIAL WAVE FUNCTION
IN ELECTRONIC WAVE FUNCTIONS

It is advantageous at this point of the development to expand the total spatial wave functions in the orthonormal set of electronic wave functions $\psi_{n\ell K}^{\tau_\phi}(\xi, \eta, \phi; \mathbf{r}_n)$ of Equation (2.26), in which i symbolizes $n, \ell, K = m_i$, and τ_ϕ of the united atom designation (Bates, Ledsham, and Stewart, 1953), n is the principal electronic quantum number, ℓ is the orbital electronic quantum number and K is the magnetic electronic quantum number. One notes that the function of the angle ϕ may be put in a form identical to that of the electronic states given in Equation (2.36),

$$\mathcal{P}_K^{\tau_\phi}(\phi) = [\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})] \cdot [\delta_{\tau_\phi,c} \cos K\phi + \delta_{\tau_\phi,s} \sin K\phi] .$$

This form is obtained, if one redefines

$$A_{LK} = \frac{A_{LK}'}{\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})} = [\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})] \sqrt{\frac{(L-K)!}{(L+K)!}} . \quad (2.40)$$

Then Equation (2.18) becomes

$$\begin{aligned} \pi_{\mu, \pi_I} \psi_0^L(\theta_n, \phi; \mathbf{r}_n, \xi, \eta) &= \sum_{K=0}^L A_{LM} P_L^K(\cos \theta) G_K^{L, \pi_I, \pi_\mu}(\mathbf{r}_n, \xi, \eta) \\ &\cdot \{ (\delta_{L, \text{even}} \delta_{\pi_I, +} + \delta_{L, \text{odd}} \delta_{\pi_I, -}) [\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})] \cos K\phi \\ &+ i (\delta_{L, \text{even}} \delta_{\pi_I, -} + \delta_{L, \text{odd}} \delta_{\pi_I, +}) [\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})] \sin K\phi \} . \quad (2.41) \end{aligned}$$

Thus, for $L = \text{even}$ and $\pi_I = +$ or $L = \text{odd}$ and $\pi_I = -$, one has

$$\pi_\mu, \pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = \sum_{K=0}^L A_{LK} P_L^K(\cos \theta_n) G_K^{L, \pi_I, \pi_\mu}(r_n, \xi, \eta) \rho_K^c(\phi). \quad (2.42)$$

For $L = \text{even}$ and $\pi_I = -$ or $L = \text{odd}$ and $\pi_I = +$, one obtains

$$\pi_\mu, \pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = \sum_{K=1}^L A_{LK} P_L^K(\cos \theta_n) G_K^{L, \pi_I, \pi_\mu}(r_n, \xi, \eta) \rho_K^s(\phi). \quad (2.43)$$

One chooses the following expansion for the total wave function:

$$\begin{aligned} \pi_\mu, \pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) &= N_L \sum_K A_{LK} P_L^K(\cos \theta_n) \sum_{n\ell} \chi_{n\ell K}^{\tau\phi}(r_n) \\ &\cdot \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) ; \end{aligned} \quad (2.44)$$

in which the product

$$G_K^{L, \pi_I, \pi_\mu}(r_n, \xi, \eta) \rho_K^{\tau\phi}(\phi) = N_L \sum_{n\ell} \chi_{n\ell K}^{\tau\phi}(r_n) \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) \quad (2.45)$$

has been expanded in a radial function $\chi_{n\ell K}^{\tau\phi}(r_n)$ and a subset of the electronic states, and N_L is a normalization constant. The muon inversion operator P_μ yields, from Equations (2.23) and (2.47),

$$P_\mu \{ G_K^{L, \pi_I, \pi_\mu}(r_n, \xi, \eta) \rho_K^{\tau\phi}(\phi) \} = \pi_\mu G_K^{L, \pi_I, \pi_\mu}(r_n, \xi, \eta) \rho_K^{\tau\phi}(\phi).$$

Since $P_\mu \chi_{n\ell K}^{\tau\phi}(r_n) = \chi_{n\ell K}^{\tau\phi}(r_n)$, one must have a definite gerade-ungerade

symmetry for the electronic states in Equation (2.45):

$$P_{\mu} \{ \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) \} = \Pi_{\mu} \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) .$$

One recalls the electronic wave function (Equation 2.27),

$$\psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) = \mathcal{N}_{n\ell K}(r_n) \Lambda_{n\ell K}(\xi, r_n) M_{n\ell K}(\eta, r_n) \mathcal{P}_K^{\tau\phi}(\phi) .$$

The muon inversion operator P_{μ} yields

$$P_{\mu} \{ \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) \} = \mathcal{N}_{n\ell K}(r_n) \Lambda_{n\ell K}(\xi, r_n) M_{n\ell K}(-\eta, r_n) \mathcal{P}_K^{\tau\phi}(\phi \pm \Pi) .$$

One obtains from Equation (2.37)

$$M_{n\ell K}(-\eta, r_n) = (-)^{\ell+K} M_{n\ell K}(\eta, r_n) \quad (2.46)$$

and from Equation (2.36)

$$\mathcal{P}_K^{\tau\phi}(\phi \pm \Pi) = (-)^K \mathcal{P}_K^{\tau\phi}(\phi) . \quad (2.47)$$

The result of muon inversion for the electronic states becomes

$$P_{\mu} \{ \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) \} = (-)^{\ell} \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n) . \quad (2.48)$$

Thus, one obtains

$$(-)^{\ell} = \Pi_{\mu} . \quad (2.49)$$

This result means that, if the total spatial wave function

$\Pi_{\mu}, \Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta)$ has gerade symmetry ($\Pi_{\mu} = +1$), the ℓ value of $M_{n\ell K}(\eta, r_n)$ must be even. Similarly, for ungerade symmetry ($\Pi_{\mu} = -1$), the ℓ value must be odd. More explicitly, the total spatial wave function $\Pi_{\mu}, \Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta)$ is expanded in gerade electronic states, if the total spatial wave function is gerade. Similarly, the total spatial wave function is expanded in ungerade electronic states, if the total spatial wave function is ungerade. Both results are contained in the expansion

$$\begin{aligned} \Pi_{\mu}, \Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) &= N_L \sum_K A_{LK} P_L^K(\cos \phi) \\ &\cdot \sum_n \sum_{(-)\ell=\Pi_{\mu}} \chi_{n\ell K}^{\tau\phi}(r_n) \psi_{n\ell K}^{\tau\phi}(\xi, \eta, \phi; r_n). \end{aligned} \quad (2.50)$$

In the following, the function $\chi_{n\ell K}^{\tau\phi}(r_n)$ is frequently transformed to

$$\phi_{n\ell K}^{\tau\phi}(r_n) = r_n \cdot \chi_{n\ell K}^{\tau\phi}(r_n). \quad (2.51)$$

Referring also to Equations (2.41) and (2.42), one has explicitly for either $L = \text{even}$ and $\Pi_I = +$ or $L = \text{odd}$ and $\Pi_I = -$

$$\begin{aligned} g, \Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) &= N_L \sum_{K=0}^L A_{LK} P_L^K(\cos \theta_n) \sum_n \sum_{\ell=\text{even}} \chi_{n\ell K}^c(r_n) \\ &\cdot \psi_{n\ell K}^c(\xi, \eta, \phi; r_n) \end{aligned} \quad (2.52)$$

and

$$u, \pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = N_L \sum_{K=0}^L A_{LK} P_L^K(\cos \theta_n) \sum_n \sum_{\ell=\text{odd}} x_{n\ell K}^c(r_n) \cdot \psi_{n\ell K}^c(\xi, \eta, \phi; r_n) \quad (2.53)$$

where the electronic states have $\cos K\phi$ dependence, as denoted by the superscript c. Similarly, for either $L = \text{even}$ and $\pi_I = -$ or $L = \text{odd}$ and $\pi_I = +$

$$g, \pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = N_L \sum_{K=1}^L A_{LK} P_L^K(\cos \theta_n) \sum_n \sum_{\ell=\text{even}} x_{n\ell K}^s(r_n) \cdot \psi_{n\ell K}^s(\xi, \eta, \phi; r_n) \quad (2.54)$$

and

$$u, \pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = N_L \sum_{K=1}^L A_{LK} P_L^K(\cos \theta_n) \sum_n \sum_{\ell=\text{odd}} x_{n\ell K}^s(r_n) \cdot \psi_{n\ell K}^s(\xi, \eta, \phi; r_n) \quad (2.55)$$

where the electronic states have $\sin K\phi$ dependence, as denoted by the superscript s.

The lowest rotational-vibrational bands obtained from the four possible expansions above are expected to arise from Equation (2.52). This equation includes the $1s\sigma_g$ and $3d\sigma_g$ electronic states, which have much lower electronic energies $W_i(r_n)$ and larger radial wave functions $\chi_i(r_n)$ than do the other electronic states. Thus, the lowest levels are expected to be the gerade total spatial wave functions having even L and even

parity Π_I or odd L and odd parity Π_I . Each of these levels is $(2L + 1)$ -fold degenerate, corresponding to the allowed values of M . Note that electronic states with non-zero magnetic quantum numbers K are required for any case except $L = 0$. For example, Π -states are required if $L = 1$ in Equation (2.52).

VIII. NORMALIZATION OF THE TOTAL SPATIAL WAVE FUNCTION

In the following, one abbreviates the expansion of the wave function by dropping the labels Π_I and Π_μ from the total wave function

$$\Pi_\mu, \Pi_I \psi_0^L(\theta_n, \phi; r_n, \xi, \eta)$$

such that it reverts to $\psi_0^L(\theta_n, \phi; r_n, \xi, \eta)$. Consequently, the limits on K are not specified and are understood to be $K = 0(1)L$ or $K = 1(1)L$, in accordance with the results of Equations (2.52) through (2.55). In long equations the arguments are dropped to shorten the expressions.

In addition, the electronic state quantum numbers n , ℓ , K , and τ_ϕ may be abbreviated by a single label i or j . Thus, one writes

$$\psi_0^L(\theta_n, \phi; r_n, \xi, \eta) = N_L \sum_K A_{LK} P_L^K(\cos \theta_n) \sum_i \chi_i(r_n) \psi_i(\xi, \eta, \phi; r_n)$$

or

$$\psi_0^L = N_L \sum_K A_{LK} P_L^K \sum_i \chi_i \psi_i \quad (2.56)$$

The normalization constant N_L is understood to be tagged by the same labels Π_I and Π_μ that label ψ_0^L . The electronic magnetic quantum number $m = K$ or K'

may be displayed explicitly, if it clarifies the derivation. The value $m_j = K$ is taken to be associated with the electronic state j and $m_i = K'$ with the state i in the following.

The functions $\psi_0^L(\theta_n, \phi; r_n, \xi, \eta)$ are normalized by requiring

$$\begin{aligned}
 1 &= \int_{r_n} d^3 r_n \int_{R_n} d^3 R_n |\psi^{v,L}|^2 \\
 &= (N_L)^2 \int d^3 r_n \int d^3 R_n \left(\sum_K A_{LK} P_L^K \sum_j \frac{\phi_j^{vLK}}{r_n} \psi_{jK} \right)^* \\
 &\quad \cdot \left(\sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{vLK'}}{r_n} \psi_{iK'} \right) = (N_L)^2 \sum_K \sum_{K'} A_{LK'} A_{LK} \\
 &\quad \cdot \int d^3 r_n P_L^{K'} P_L^K \sum_j \sum_i \frac{\phi_j^{vLK}}{r_n} \frac{\phi_i^{vLK'}}{r_n} \int d^3 R_n \psi_{jK} \psi_{iK'} \quad , \quad (2.57)
 \end{aligned}$$

where v labels the vibrational quantum number. From Equation (B.3)

$$\int d^3 R_n \psi_{jK} \psi_{iK'} = \delta_{j,i} \delta_{K,K'} \quad , \quad (2.58)$$

and one has, with $x = \cos \theta$,

$$1 = (N_L)^2 \sum_K (A_{LK})^2 \int_0^{2\pi} d\phi \int_{-1}^1 dx [P_L^K(x)]^2 \sum_j \int_0^\infty dr_n [\phi_j^{vLK}]^2 \quad .$$

Noting that $(A_{LK})^2 = (2-\delta_{K,0}) \left[\frac{(L-K)!}{(L+K)!} \right]$ and $\int dx [P_L^K(x)]^2 = \frac{2}{2L+1} \cdot \frac{(L+K)!}{(L-K)!}$,

the above becomes

$$\begin{aligned}
1 &= (N_L)^2 \sum_K (2-\delta_{K,0}) \cdot (2\pi) \cdot \left[\frac{2}{2L+1} \cdot \sum_j \int_0^\infty dr_n [\phi_j^{LK}]^2 \right] \\
&= (N_L)^2 \frac{4\pi}{2L+1} \sum_K (2-\delta_{K,0}) \sum_j \int_0^\infty dx [\phi_j^{LK}]^2 .
\end{aligned}$$

One thus requires

$$N_L = \sqrt{\frac{2L+1}{4\pi}} \quad (2.59)$$

and

$$\sum_K (2-\delta_{K,0}) \sum_j \int_0^\infty dr_n [\phi_j^{LK}]^2 = 1 \quad (2.60)$$

The summations and integration commute, so the latter can be written as

$$\int_0^\infty dr_n \left\{ \sum_K (2-\delta_{K,0}) \sum_j [\phi_j^{LK}]^2 \right\} = 1. \quad (2.61)$$

In practice, the maximum number of elements ϕ_j^{LK} that could be included in a calculation on the IBM 7090 computer was limited to six, due to storage limitations of the computer and the execution time required.

IX. DERIVATION OF COUPLED EQUATIONS AND COUPLING PARAMETERS

One has obtained

$$\begin{aligned}
\psi_L^0(\theta_n, \phi; r_n, \xi, \eta) &= N_L \sum_{K'} A_{LK'} P_L^{K'}(\cos \theta_n) \sum_i x_i^{LK'}(r_n) \\
&\cdot \psi_{iK'}(\xi, \eta, \phi; r_n) ,
\end{aligned} \quad (2.56)$$

where

$$A_{LK'} = [\delta_{K,0} + \sqrt{2} \cdot (1 - \delta_{K,0})] \sqrt{\frac{(L-K')!}{(L+K')!}} \quad (2.40)$$

Let

$$x_i^{LK'}(r_n) = \frac{\phi_i^{LK'}(r_n)}{r_n} \quad (2.51)$$

then

$$\psi_0^L = N_L \sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \psi_{iK'} \quad (2.62)$$

From Equation (2.25), where $H_\mu = -\nabla_\mu^2 - \frac{2}{r_{\mu 1}} - \frac{2}{r_{\mu 2}}$,

$$\begin{aligned} H_\mu \psi_0^L &= N_L \sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} H_\mu \psi_{iK'} \\ &= N_L \sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} W_{iK'} \psi_{iK'} \quad (2.63) \end{aligned}$$

Substitution of ψ_0^L in Equation (2.5) yields

$$\left\{ -\epsilon \nabla_n^2 + \frac{2}{r_n} + H_\mu - E \right\} N_L \sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \psi_{iK'} = 0 \quad ,$$

where $\epsilon = \frac{M_\mu}{M_n} = \frac{4m_\mu}{2m_p + m_\mu}$ (Equation 2.6). Then

$$N_L \left\{ \nabla_n^2 - \frac{1}{\epsilon} \left(\frac{2}{r_n} + H_\mu - E \right) \right\} \sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \psi_{iK'} = 0 \quad .$$

Expanding the above, one has

$$\sum_{K'} A_{LK'} \left\{ \left[\nabla_n^2 \left(p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \right) \right] \psi_{iK'} + 2 \left[\vec{\nabla}_n \left(p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \right) \right] \cdot \vec{\nabla}_n \psi_{iK'} + p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \left[\nabla_n^2 \psi_{iK'} - \frac{1}{\epsilon} \left(\frac{2}{r_n} + W_{iK'} - E \right) \psi_{iK'} \right] \right\} = 0. \quad (2.64)$$

Multiplication on the left by ψ_{jK} and integration over the muon space

$$d^3 R_\mu = \frac{r_n^3 (\xi^2 - \eta^2)}{8} d\xi d\eta d\phi \text{ yields}$$

$$\sum_{K'} A_{LK'} \left\{ \left[\nabla_n^2 \left(p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \right) \delta_{j,i} \delta_{K',K} + 2 \left[\vec{\nabla}_n \left(p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \right) \right] \cdot \int_{R_\mu} \psi_{jK} \vec{\nabla}_n \psi_{iK'} d^3 R_\mu + p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \left[\int_{R_\mu} \psi_{jK} \nabla_n^2 \psi_{iK} d^3 R_\mu - \frac{(V_{iK'} - E)}{\epsilon} \delta_{j,i} \delta_{K',K} \right] \right\} = 0, \quad (2.65)$$

$$\text{where } V_{iK'}(r_n) = \frac{2}{r_n} + W_{iK'}(r_n). \quad (2.66)$$

Cohen, Judd, and Riddell (1960a) defined a coupling vector

$$\vec{f}_{jK,iK'} = \int_{R_\mu} \psi_{jK} \vec{\nabla}_n \psi_{iK'} d^3 R_\mu \quad (2.67)$$

and a coupling scalar

$$g_{jK,iK'} = \int_{R_\mu} (\vec{\nabla}_n \psi_{jK}) \cdot (\vec{\nabla}_n \psi_{iK'}) d^3 R_\mu. \quad (2.68)$$

From a vector identity one obtains

$$\int_{R_\mu} \psi_{jK} \nabla_n^2 \psi_{iK} d^3 R_\mu = \int_{R_\mu} \vec{\nabla}_n \cdot (\psi_{jK} \vec{\nabla}_n \psi_{iK}) - (\vec{\nabla}_n \psi_{jK}) \cdot (\vec{\nabla}_n \psi_{iK}) d^3 R_\mu = \vec{\nabla}_n \cdot \vec{f}_{jK, iK} - g_{jK, iK} \quad (2.69)$$

Substitution in Equation (2.65) yields

$$A_{LK} \left\{ \nabla_n^2 \left[p_L^K \frac{\phi_j^{LK}}{r_n} \right] - \frac{(V_j^K - E)}{\epsilon} p_L^K \frac{\phi_j^{LK}}{r_n} \right\} + \sum_{K'} A_{LK'} \left\{ 2 \left[\vec{\nabla}_n \left(p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \right) \right] \cdot \vec{f}_{jK, iK'} + p_L^{K'} \sum_i \frac{\phi_i^{K'}}{r_n} [\vec{\nabla}_n \cdot \vec{f}_{jK, iK'} - g_{jK, iK'}] \right\} = 0 \quad (2.70)$$

Since there is no dependence of $\phi_j^{LK}(r_n)$ or $p_L^K(\cos \theta_n)$ on the angular variable ϕ_n , one obtains for the first term

$$\nabla_n^2 \left[p_L^K \frac{\phi_i^{LK}}{r_n} \right] = \frac{1}{r_n} \left[p_L^K \frac{d^2 \phi_j^{LK}}{dr_n^2} + \frac{1}{r_n^2} \left(\frac{d^2 p_L^K}{d\theta_n^2} + \frac{1}{\tan \theta_n} \frac{dp_L^K}{d\theta_n} \right) \phi_j^{LK} \right] \quad (2.71)$$

Also, one obtains

$$\left[\vec{\nabla}_n \left(p_L^{K'} \sum_i \frac{\phi_i^{LK'}}{r_n} \right) \right] \cdot \vec{f}_{jK, iK'} = \frac{1}{r_n} \left\{ p_L^{K'} \sum_i \left[\frac{d\phi_i^{LK'}}{dr_n} - \phi_i^{LK'} \right] Q_{jK, iK'} + \frac{1}{r_n} \frac{dp_L^{K'}}{d\theta_n} \sum_i \phi_i^{LK'} \cdot \frac{1}{r_n} U_{jK, iK'} \right\} \quad (2.72)$$

where two coupling parameters are defined as

$$Q_{jK,iK'} = \hat{e}_{r_n} \cdot \vec{f}_{jK,iK'} \quad (2.73)$$

and

$$J_{jK,iK'} = \hat{e}_{\phi_n} \cdot \vec{f}_{jK,iK'} \quad (2.74)$$

The term involving the divergence of the coupling vector is

$$\begin{aligned} p_L^{K'} \sum_i \frac{\phi_i^{K'}}{r_n} \vec{\nabla}_n \cdot \vec{f}_{jK,iK'} &= \frac{1}{r_n} p_L^{K'} \sum_i \phi_i^{LK'} \\ &\cdot \left[\left(\frac{\partial}{\partial r_n} + \frac{2}{r_n} \right) Q_{jK,iK'} + \left(\frac{1}{r_n} \frac{\partial}{\partial \theta_n} + \frac{1}{r_n \tan \theta_n} \right) \left(\frac{1}{r_n} J_{jK,iK'} \right) \right. \\ &\left. + \left(\frac{1}{r_n \sin \theta_n} \frac{\partial}{\partial \phi_n} \right) \left(\frac{1}{r_n \sin \theta_n} P_{jK,iK'} \right) \right] \quad (2.75) \end{aligned}$$

where the last coupling parameter is defined as

$$P_{jK,iK'} = \hat{e}_{\phi_n} \cdot \vec{f}_{jK,iK'} \quad (2.76)$$

Substitution of the above expressions in Equation (2.70) yields

$$\begin{aligned} \frac{1}{r_n} A_{LK} \left\{ p_L^K \left[\frac{d^2 \phi_j^{LK}}{dr_n^2} - \frac{(V_j^K - E)}{\epsilon} \phi_j^{LK} \right] + \frac{1}{r_n^2} \left(\frac{d^2 p_L^K}{d\theta_n^2} + \frac{1}{\tan \theta_n} \frac{dp_L^K}{d\theta_n} \right) \phi_j^{LK} \right\} \\ + \frac{1}{r_n} \sum_{K'} A_{LK'} \left\{ p_L^{K'} \sum_i \left[2 Q_{jK,iK'} \frac{d\phi_i^{LK'}}{dr_n} + \left(\frac{\partial Q_{jK,iK'}}{\partial r_n} + \frac{J_{jK,iK'}}{r_n^2 \tan \theta_n} \right. \right. \right. \\ \left. \left. + \frac{1}{r_n^2} \frac{\partial J_{jK,iK'}}{\partial \theta_n} - g_{jK,iK'} \right) \phi_i^{LK'} \right] + \frac{1}{r_n^2} \frac{dp_L^{K'}}{d\theta_n} \sum_i 2 J_{jK,iK'} \phi_i^{LK'} \right\} = 0, \quad (2.77) \end{aligned}$$

where the coupling parameters have been defined as

$$Q_{jK,iK'} = \hat{e}_{r_n} \cdot \vec{f}_{jK,iK'} = \hat{e}_{r_n} \cdot \int_{R_\mu} \psi_{jK} \vec{\nabla}_n \psi_{iK'} d^3R_\mu, \quad (2.73)$$

$$J_{jK,iK'} = \hat{e}_{\theta_n} \cdot \vec{f}_{jK,iK'} = \hat{e}_{\theta_n} \cdot \int_{R_\mu} \psi_{jK} \vec{\nabla}_n \psi_{iK'} d^3R_\mu, \quad (2.74)$$

$$P_{jK,iK'} = \hat{e}_{\phi_n} \cdot \vec{f}_{jK,iK'} = \hat{e}_{\phi_n} \cdot \int_{R_\mu} \psi_{jK} \vec{\nabla}_n \psi_{iK'} d^3R_\mu, \quad (2.76)$$

and

$$g_{jK,iK'} = \int_{R_\mu} (\vec{\nabla}_n \psi_{jK}) \cdot (\vec{\nabla}_n \psi_{iK'}) d^3R_\mu. \quad (2.68)$$

Further reduction of the coupled equations must be deferred until the angular dependence of the coupling parameters has been established. The form of the coupling parameters is obtained in the next section, along with the symmetry of each one with respect to interchange of the indices jK and iK' . Reduction of the coupled equations is continued on page 72.

X. EVALUATION OF THE COUPLING PARAMETERS FOR EQUAL-MASS (HOMONUCLEAR) CASE

Evaluation of the coupling parameters requires detailed calculation of certain geometric properties of the three-body system. These geometric properties are derived in Appendix A and are applied below to the evaluation of the coupling parameters for the equal-mass (homonuclear) case. Basic to this evaluation is the equivalence of the following expressions:

$$\vec{\nabla}_n \psi_{iK'}(\xi, \eta, \phi; r_n) = \frac{\partial \psi_{iK'}}{\partial r_n} \vec{\nabla}_n(r_n) + \frac{\partial \psi_{iK'}}{\partial \xi} \vec{\nabla}_n(\xi) + \frac{\partial \psi_{iK'}}{\partial \eta} \vec{\nabla}_n(\eta) + \frac{\partial \psi_{iK'}}{\partial \phi} \vec{\nabla}_n(\phi) \quad (2.78)$$

$$= \frac{\delta \psi_{iK'}}{\delta r_n} \hat{e}_{r_n} + \frac{1}{r_n} \frac{\delta \psi_{iK'}}{\delta \theta_n} \hat{e}_{\theta_n} + \frac{1}{r_n \sin \theta_n} \frac{\delta \psi_{iK'}}{\delta \phi_n} \hat{e}_{\phi_n}, \quad (2.79)$$

where

$$\frac{\delta}{\delta r_n} = \frac{\partial}{\partial r_n} + \frac{\partial \xi}{\partial r_n} \frac{\partial}{\partial \xi} + \frac{\partial \eta}{\partial r_n} \frac{\partial}{\partial \eta}, \quad (2.80)$$

$$\frac{\delta}{\delta \theta_n} = \frac{\partial \xi}{\partial \theta_n} \frac{\partial}{\partial \xi} + \frac{\partial \eta}{\partial \theta_n} \frac{\partial}{\partial \eta} + \frac{\partial \phi}{\partial \theta_n} \frac{\partial}{\partial \phi}, \quad (2.81)$$

and

$$\frac{\delta}{\delta \phi_n} = \frac{\partial \xi}{\partial \phi_n} \frac{\partial}{\partial \xi} + \frac{\partial \eta}{\partial \phi_n} \frac{\partial}{\partial \eta} + \frac{\partial \phi}{\partial \phi_n} \frac{\partial}{\partial \phi}. \quad (2.82)$$

Recognizing that $\vec{\nabla}_n(r_n) = \hat{e}_{r_n}$ and using the equal-mass results obtained

in Appendix A, one has from Equation (A.4)

$$\vec{\nabla}_n(\xi) = \frac{-\frac{1}{2} \hat{e}_{r_{\mu 1}} + \frac{1}{2} \hat{e}_{r_{\mu 2}} - \xi \hat{e}_{r_n}}{r_n}, \quad (2.83)$$

from Equation (A.19)

$$\vec{\nabla}_n(\eta) = \frac{-\frac{1}{2} \hat{e}_{r_{\mu 1}} - \frac{1}{2} \hat{e}_{r_{\mu 2}} - \eta \hat{e}_{r_n}}{r_n}, \quad (2.84)$$

and from Equation (A.20)

$$\vec{\nabla}_n(\phi) = \frac{\partial \phi}{\partial \theta_n} \frac{\hat{e}_{\theta_n}}{r_n} + \frac{\partial \phi}{\partial \phi_n} \frac{\hat{e}_{\phi_n}}{r_n \sin \phi_n}. \quad (2.85)$$

It is shown (Equation A.11) that

$$\begin{aligned} \hat{e}_{r_{\mu 1}} = & \frac{1}{\xi + \eta} \left\{ \sqrt{(\xi^2 - 1)(1 - \eta^2)} (\cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}) \right. \\ & \left. - (\xi \eta + 1) \hat{e}_{r_n} \right\} \end{aligned} \quad (2.86)$$

and (Equation A.17)

$$\begin{aligned} \hat{e}_{r_{\mu 2}} = & \frac{1}{\xi - \eta} \left\{ \sqrt{(\xi^2 - 1)(1 - \eta^2)} (\cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}) \right. \\ & \left. - (\xi \eta - 1) \hat{e}_{r_n} \right\} . \end{aligned} \quad (2.87)$$

One obtains for the equal-mass case (cf. Equations A.38, A.39, and A.40)

$$\begin{aligned} \vec{v}_n(\xi) = & \frac{1}{r_n(\xi^2 - \eta^2)} \left\{ \sqrt{(\xi^2 - 1)(1 - \eta^2)} \eta \cdot (\cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}) \right. \\ & \left. - \xi(\xi^2 - 1) \hat{e}_{r_n} \right\} , \end{aligned} \quad (2.88)$$

$$\begin{aligned} \vec{v}_n(\eta) = & - \frac{1}{r_n(\xi^2 - \eta^2)} \left\{ \sqrt{(\xi^2 - 1)(1 - \eta^2)} \xi \cdot (\cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}) \right. \\ & \left. + \eta(1 - \eta^2) \hat{e}_{r_n} \right\} , \end{aligned} \quad (2.89)$$

and

$$\vec{v}_n(\phi) = \left(- \frac{\xi \eta}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \sin \phi \right) \hat{e}_{\theta_n} + \left(\frac{\xi \eta}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \cos \phi \right)$$

$$- \frac{1}{r_n \tan \theta_n} \Big) \hat{e}_{\phi_n} \quad (2.90)$$

Thus, one has for the equal-mass case

$$\begin{aligned} \vec{\nabla}_n \psi_{iK'} = & \left\{ \frac{\partial \psi_{iK'}}{\partial r_n} - \frac{\xi(\xi^2-1)}{r_n(\xi^2-n^2)} \frac{\partial \psi_{iK'}}{\partial \xi} - \frac{n(1-n^2)}{r_n(\xi^2-n^2)} \frac{\partial \psi_{iK'}}{\partial n} \right\} \hat{e}_{r_n} \\ & + \left\{ \frac{\sqrt{(\xi^2-1)(1-n^2)}}{r_n(\xi^2-n^2)} \cos \phi \cdot \left(\eta \frac{\partial \psi_{iK'}}{\partial \xi} - \xi \frac{\partial \psi_{iK'}}{\partial n} \right) \right. \\ & \left. - \frac{\xi n}{r_n \sqrt{(\xi^2-1)(1-n^2)}} \sin \phi \frac{\partial \psi_{iK'}}{\partial \phi} \right\} \hat{e}_{\theta_n} \\ & + \left\{ \frac{\sqrt{(\xi^2-1)(1-n^2)}}{r_n(\xi^2-n^2)} \cdot \sin \phi \left(\eta \frac{\partial \psi_{iK'}}{\partial \xi} - \xi \frac{\partial \psi_{iK'}}{\partial n} \right) \right. \\ & \left. + \left(\frac{\xi n}{r_n \sqrt{(\xi^2-1)(1-n^2)}} \cos \phi - \frac{1}{r_n \tan \theta_n} \right) \frac{\partial \psi_{iK'}}{\partial \phi} \right\} \hat{e}_{\phi_n} \quad (2.91) \end{aligned}$$

From which one may write

$$\frac{\partial \xi}{\partial r_n} = - \frac{\xi(\xi^2-1)}{r_n(\xi^2-n^2)} \quad (2.92)$$

$$\frac{\partial n}{\partial r_n} = - \frac{n(1-n^2)}{r_n(\xi^2-n^2)} \quad (2.93)$$

$$\frac{1}{r_n} \frac{\partial \xi}{\partial \theta_n} = \frac{\eta \sqrt{(\xi^2-1)(1-n^2)} \cos \phi}{r_n(\xi^2-n^2)} \quad (2.94)$$

$$\frac{1}{r_n} \frac{\partial \eta}{\partial \theta_n} = - \frac{\xi \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \phi}{r_n (\xi^2 - \eta^2)} , \quad (2.95)$$

$$\frac{1}{r_n} \frac{\partial \phi}{\partial \theta_n} = - \frac{\xi \eta}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \sin \phi , \quad (2.96)$$

$$\frac{1}{r_n \sin \theta_n} \frac{\partial \xi}{\partial \phi_n} = \frac{\eta \sqrt{(\xi^2 - 1)(1 - \eta^2)}}{r_n (\xi^2 - \eta^2)} \sin \phi , \quad (2.97)$$

$$\frac{1}{r_n \sin \theta_n} \frac{\partial \eta}{\partial \phi_n} = - \frac{\xi \sqrt{(\xi^2 - 1)(1 - \eta^2)}}{r_n (\xi^2 - \eta^2)} \sin \phi , \quad (2.98)$$

and

$$\frac{1}{r_n \sin \theta_n} \frac{\partial \phi}{\partial \phi_n} = \frac{\xi \eta}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \cos \phi - \frac{1}{r_n \tan \theta_n} . \quad (2.99)$$

The above results demonstrate the resolution of $\vec{\nabla}_n \psi_{iK}$ as given in Equation (2.78) into the orthogonal components given in Equation (2.79). These results are used below to calculate the coupling parameters. It is recognized that the operator $\frac{\partial}{\partial r_n} \rightarrow \frac{\delta}{\delta r_n}$ when it operates on a function of the muon coordinates r_n , ξ , η , and ϕ . Similarly, $\frac{\partial}{\partial \theta_n} \rightarrow \frac{\delta}{\delta \theta_n}$ and $\frac{\partial}{\partial \phi_n} \rightarrow \frac{\delta}{\delta \phi_n}$.

Thus, the quantity $Q_{jK, iK'}$ for equal nuclear mass becomes (Equations 2.73, 2.80, 2.92, and 2.93)

$$Q_{jK, iK'} = \int_{R_\mu} \psi_{jK} \frac{\delta}{\delta r_n} \psi_{iK'} d^3 R_\mu$$

$$\begin{aligned}
&= \int_{\xi=1}^{\infty} \int_{\eta=-1}^1 \int_{\phi=0}^{2\pi} \psi_{jK} \cdot \left\{ \frac{\partial \psi_{iK'}}{\partial r_n} - \frac{\xi(\xi^2-1)}{r_n(\xi^2-\eta^2)} \frac{\partial \psi_{iK'}}{\partial \xi} \right. \\
&\quad \left. - \frac{\eta(1-\eta^2)}{r_n(\xi^2-\eta^2)} \frac{\partial \psi_{iK'}}{\partial \eta} \right\} \cdot \frac{r_n^3(\xi^2-\eta^2)}{8} d\xi d\eta d\phi . \quad (2.100)
\end{aligned}$$

Using $\psi_{iK'}(\xi, \eta, \phi; r_n) = \mathcal{N}_i(r_n) \Lambda_i(\xi, r_n) M_i(\eta, r_n) \rho_{K'}^{\tau\phi}(\phi)$ (Equation 2.27),

the following results are obtained:

$$\frac{\partial \psi_{iK'}}{\partial r_n} = \left\{ \frac{d\mathcal{N}_i}{dr_n} \Lambda_i M_i + \mathcal{N}_i \left[\frac{\partial \Lambda_i}{\partial r_n} M_i + \Lambda_i \frac{\partial M_i}{\partial r_n} \right] \right\} \cdot \rho_{K'}^{\tau\phi} , \quad (2.101)$$

$$\frac{\partial \psi_{iK'}}{\partial \xi} = \mathcal{N}_i \frac{\partial \Lambda_i}{\partial \xi} M_i \rho_{K'}^{\tau\phi} , \quad (2.102)$$

and

$$\frac{\partial \psi_{iK'}}{\partial \eta} = \mathcal{N}_{iK'} \Lambda_{iK'} \frac{\partial M_{iK'}}{\partial \eta} \rho_{K'}^{\tau\phi} . \quad (2.103)$$

Referring to Equation (2.38), one has

$$\frac{\partial \Lambda_{iK'}}{\partial r_n} = \Lambda_{iK'} \left\{ \ln(\xi+1) \frac{d\sigma_{iK'}(r_n)}{dr_n} - \xi \frac{dp_{iK'}(r_n)}{dr_n} + \frac{\sum_{t=0}^{\infty} \left[\frac{dg_t^{(i)}(r_n)}{dr_n} \right] \zeta^t}{y_i(\zeta, r_n)} \right\} . \quad (2.104)$$

From Equation (2.37) one obtains

$$\frac{\partial M_{iK'}}{\partial r_n} = \sum_{n=0,1}^{\infty} \left[\frac{df_n^{(i)}(r_n)}{dr_n} \right] P_{K'+n}^{K'(n)} . \quad (2.105)$$

Similarly, one may calculate

$$\frac{\partial \Lambda_{iK'}}{\partial \xi} = \Lambda_{iK'} \cdot \left\{ \frac{K' \xi}{(\xi^2 - 1)} + \frac{\sigma_{iK'}(r_n)}{\xi + 1} - p_{iK'}(r_n) + \frac{2}{(\xi + 1)^2} \right. \\ \left. \cdot \frac{\sum_{t=1}^{\infty} t \cdot g_t^{(i)}(r_n) \cdot \zeta^{t-1}}{y_i(\zeta, r_n)} \right\}, \quad (2.106)$$

and

$$\frac{\partial M_{iK'}}{\partial \eta} = \sum_{n=0,1}^{\infty} f_n^{(i)}(r_n) \frac{\partial p_{K'+n}^{K'}(\eta)}{\partial \eta}. \quad (2.107)$$

In the above expressions the derivatives with respect to r_n of the normalization constant $\mathcal{N}_{iK'}(r_n)$, the parameters $\sigma_{iK'}(r_n)$ and $p_{iK'}(r_n)$, and the expansion coefficients $g_t^{(i)}(r_n)$ and $f_n^{(i)}(r_n)$ must be calculated numerically.

Recalling from Equations (2.52) through (2.55) that a total spatial wave function for the homonuclear (equal-mass) case has a constant value of τ_ϕ , one does not need to consider coupling between $\cos K\phi$ and $\sin K\phi$ functions. Performing the integral over the variable ϕ yields, for $\tau_\phi = c$,

$$\int_0^{2\pi} \mathcal{P}_K^c(\phi) \mathcal{P}_{K'}^c(\phi) d\phi = 2\pi \delta_{K,K'}. \quad (B.7)$$

Thus,

$$\mathcal{Q}_{j,K;i,K'}(r_n) = 2\pi \mathcal{Q}_{j,K,iK'}^{(1)}(r_n) \delta_{K,K'} \quad (2.108)$$

where

$$\begin{aligned} Q_{j,K;i,K'}^{(1)}(r_n) = \frac{r_n^3}{8} \int_{\xi=1}^{\infty} \int_{\eta=-1}^1 F_{j,K} \left\{ \frac{\partial F_{i,K'}}{\partial r_n} - \frac{\xi(\xi^2-1)}{r_n(\xi^2-\eta^2)} \cdot \frac{\partial F_{i,K'}}{\partial \xi} \right. \\ \left. - \frac{\eta(1-\eta^2)}{r_n(\xi^2-\eta^2)} \frac{\partial F_{i,K'}}{\partial \eta} \right\} \cdot (\xi^2-\eta^2) d\xi d\eta, \end{aligned} \quad (2.109)$$

$$\text{in which } F_{jK}(\xi, \eta; r_n) = \mathcal{N}_{jK}(r_n) \cdot \Lambda_{jK}(\xi, r_n) \cdot M_{jK}(\eta, r_n). \quad (2.110)$$

One obtains a similar result for $\tau_\phi = s$:

$$Q_{jK,iK'}(r_n) = 2\pi \cdot Q_{jK,iK'}^{(1)}(r_n) \cdot (1-\delta_{K,0})(1-\delta_{K',0})\delta_{K,K'}, \quad (2.111)$$

where

$$Q_{jK,iK'}^{(1)}(r_n) \text{ has been defined above (Equation 2.109).}$$

In the above one has established that the coupling parameter $Q_{jK,iK'}$ is a function only of the scalar r_n and that it only couples electronic states having the same magnetic electronic quantum number.

Consider now the coupling parameter $\mathcal{J}_{jK,iK'}$. From Equations (2.74), (2.81), (2.94), and (2.96) one has

$$\mathcal{J}_{jK,iK'} = \int_R \psi_{jK} \frac{\delta}{\delta \theta_n} \psi_{iK'} d^3 R_\mu$$

$$\begin{aligned}
&= \int_{R_\mu} \psi_{jK} \left\{ \frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{(\xi^2-\eta^2)} \cos \phi \cdot \left[\eta \frac{\partial \psi_{iK'}}{\partial \xi} - \xi \frac{\partial \psi_{iK'}}{\partial \eta} \right] \right. \\
&\quad \left. - \frac{\xi \eta}{\sqrt{(\xi^2-1)(1-\eta^2)}} \sin \phi \frac{\partial \psi_{iK'}}{\partial \phi} \right\} d^3 R_\mu.
\end{aligned} \tag{2.112}$$

In addition to the previous derivatives, one needs

$$\frac{\partial \psi_{iK'}}{\partial \phi} = \eta_{i,K'} \Lambda_{i,K'} M_{i,K'} \frac{d\varphi_{K'}^{\tau_\phi}}{d\phi} \tag{2.113}$$

and

$$\frac{d\varphi_{K'}^{\tau_\phi}}{d\phi} = \begin{cases} 0, & K' = 0 \\ \text{or} \\ \begin{cases} -\sqrt{2} \cdot K' \cdot \sin K' \phi, & \tau_\phi = c \\ \sqrt{2} \cdot K' \cdot \cos K' \phi, & \tau_\phi = s \end{cases} & K' \neq 0 \end{cases} \tag{2.114}$$

One obtains, for $\tau_\phi = c$,

$$\begin{aligned}
J_{j,K;i,K'}(r_n) &= \Pi \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K',0}) + (1-\delta_{K,0})(1-\delta_{K',0})] \\
&\cdot \left\{ J_{j,K;i,K'}^{(1)}(r_n) \cdot (\delta_{K,K'-1} + \delta_{K,K'+1}) + K' \cdot J_{j,K,iK'}^{(2)}(r_n) \right. \\
&\quad \left. \cdot (\delta_{K,K'-1} - \delta_{K,K'+1}) \right\},
\end{aligned} \tag{2.115}$$

where, letting $F_{jK}(\xi, \eta; r_n) = \eta_{jK}(r_n) \Lambda_{jK}(\xi, r_n) M_{jK}(\eta, r_n)$, (2.110)

$$\begin{aligned}
J_{jK,iK'}^{(1)}(r_n) &= \frac{r_n^3}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta \cdot (\xi^2 - \eta^2) \cdot F_{jK} \cdot \frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{(\xi^2-\eta^2)} \\
&\cdot \left[\eta \frac{\partial F_{iK'}}{\partial \xi} - \xi \frac{\partial F_{iK'}}{\partial \eta} \right]
\end{aligned} \tag{2.116}$$

and

$$\mathcal{J}_{jK, iK'}^{(2)}(r_n) = \frac{r_n^3}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta \cdot (\xi^2 - \eta^2) \cdot F_{jK} \cdot \frac{\xi\eta}{\sqrt{(\xi^2-1)(1-\eta^2)}} \cdot F_{iK'} \quad (2.117)$$

Similarly, one obtains, for $\tau_\phi = s$,

$$\begin{aligned} \mathcal{J}_{jK, iK'}(r_n) &= \Pi \cdot (1 - \delta_{K,0}) \cdot (1 - \delta_{K',0}) \cdot \{ \mathcal{J}_{jK, iK'}^{(1)}(r_n) \cdot \\ &\cdot (\delta_{K, K'-1} + \delta_{K, K'+1}) + K' \cdot \mathcal{J}_{jK, iK'}^{(2)}(r_n) \cdot (\delta_{K, K'-1} - \delta_{K, K'+1}) \} \quad (2.118) \end{aligned}$$

One notes that $\mathcal{J}_{jK, iK'} = \mathcal{J}_{jK, iK'}(r_n)$, so that

$$\frac{\partial}{\partial \theta_n} \mathcal{J}_{jK, iK'}(r_n) = 0 \quad (2.119)$$

In general, $\mathcal{J}_{jK, iK'}(r_n)$ couples electronic states which differ by unity in the magnetic electronic quantum number.

The coupling parameter $\mathcal{P}_{jK, iK'}$ may be calculated from Equations (2.76), (2.82), (2.97), (2.98), and (2.99):

$$\begin{aligned} \mathcal{P}_{jK, iK'} &= \int_{R_\mu} \psi_{jK} \frac{\delta}{\delta \phi_n} \psi_{iK'} d^3 R_\mu \\ &= \int_{R_\mu} \psi_{jK} \sin \theta_n \cdot \left\{ \frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{(\xi^2-\eta^2)} \sin \phi \left[\eta \frac{\partial \psi_{iK'}}{\partial \xi} - \xi \frac{\partial \psi_{iK'}}{\partial \eta} \right] \right. \\ &\quad \left. + \left[\frac{\xi\eta}{\sqrt{(\xi^2-1)(1-\eta^2)}} \cos \phi - \frac{1}{\tan \theta_n} \right] \frac{\partial \psi_{iK'}}{\partial \phi} \right\} d^3 R_\mu \quad (2.120) \end{aligned}$$

Note that there is a great similarity between $\mathcal{J}_{jK,iK'}$ and $\mathcal{P}_{jK,iK'}$ in the variables ξ and η . From the above equation $\mathcal{P}_{jK,iK'} = \mathcal{P}_{jK,iK'}(r_n, \theta_n)$, so

$$\frac{\partial \mathcal{P}_{jK,iK'}}{\partial \phi_n} = 0. \quad (2.121)$$

Thus, $\mathcal{P}_{jK,iK}$ does not occur in the coupled differential equations specialized to $M = 0$.

The coupling parameter $g_{jK,iK'}$ has the most lengthly expansion

(Equations 2.68 and 2.79):

$$\begin{aligned} g_{jK,iK'} &= \int_{R_\mu} (\vec{\nabla}_n \psi_{jK}) \cdot (\vec{\nabla}_n \psi_{iK'}) d^3 R_\mu \\ &= \int_{R_\mu} d^3 R_\mu \left\{ \frac{\partial \psi_{jK}}{\partial r_n} - \frac{\xi(\xi^2-1)}{r_n(\xi^2-\eta^2)} \frac{\partial \psi_{jK}}{\partial \xi} - \frac{\eta(1-\eta^2)}{r_n(\xi^2-\eta^2)} \frac{\partial \psi_{jK}}{\partial \eta} \right\} \\ &\quad \cdot \left[\frac{\partial \psi_{iK'}}{\partial r_n} - \frac{\xi(\xi^2-1)}{r_n(\xi^2-\eta^2)} \frac{\partial \psi_{iK'}}{\partial \xi} - \frac{\eta(1-\eta^2)}{r_n(\xi^2-\eta^2)} \frac{\partial \psi_{iK'}}{\partial \eta} \right] \\ &\quad + \left[\frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{r_n(\xi^2-\eta^2)} \cos \phi \left(\eta \frac{\partial \psi_{jK}}{\partial \xi} - \xi \frac{\partial \psi_{jK}}{\partial \eta} \right) - \frac{\xi \eta}{r_n \sqrt{(\xi^2-1)(1-\eta^2)}} \right. \\ &\quad \cdot \left. \sin \phi \frac{\partial \psi_{jK}}{\partial \phi} \right] \cdot \left[\frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{r_n(\xi^2-\eta^2)} \cos \phi \left(\eta \frac{\partial \psi_{iK'}}{\partial \xi} - \xi \frac{\partial \psi_{iK'}}{\partial \eta} \right) \right. \\ &\quad \cdot \left. - \frac{\xi \eta}{r_n \sqrt{(\xi^2-1)(1-\eta^2)}} \sin \phi \frac{\partial \psi_{iK'}}{\partial \phi} \right] + \left[\frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{r_n(\xi^2-\eta^2)} \sin \phi \right. \\ &\quad \cdot \left. \left(\eta \frac{\partial \psi_{jK}}{\partial \xi} - \xi \frac{\partial \psi_{jK}}{\partial \eta} \right) + \left(\frac{\xi \eta}{r_n \sqrt{(\xi^2-1)(1-\eta^2)}} \cos \phi - \frac{1}{r_n \tan \theta_n} \right) \right] \end{aligned}$$

$$\begin{aligned}
& \cdot \frac{\partial \psi_{jK}}{\partial \phi} \cdot \left[\frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{r_n(\xi^2-\eta^2)} \sin \phi \left(\eta \frac{\partial \psi_{iK'}}{\partial \xi} - \xi \frac{\partial \psi_{iK'}}{\partial \eta} \right) \right. \\
& \left. + \left(\frac{\xi \eta}{r_n \sqrt{(\xi^2-1)(1-\eta^2)}} \cos \phi - \frac{1}{r_n \tan \theta_n} \right) \frac{\partial \psi_{iK'}}{\partial \phi} \right] \} . \quad (2.122)
\end{aligned}$$

This result can be put in a shorter form using the identity

$$\xi^2(\xi^2-1) + \eta^2(1-\eta^2) = (\xi^2-\eta^2)(\xi^2+\eta^2-1) \quad (2.123)$$

and trigonometric identities:

$$\begin{aligned}
g_{jK,iK'} &= \int_{R_\mu} d^3 R_\mu \left\{ \frac{\partial \psi_{jK}}{\partial r_n} \frac{\partial \psi_{iK'}}{\partial r_n} + \frac{\xi^2+\eta^2-1}{r_n^2(\xi^2-\eta^2)} \left[(\xi^2-1) \frac{\partial \psi_{jK}}{\partial \xi} \frac{\partial \psi_{iK'}}{\partial \xi} \right. \right. \\
&+ (1-\eta^2) \frac{\partial \psi_{jK}}{\partial \eta} \frac{\partial \psi_{iK'}}{\partial \eta} \left. \right] - \frac{\xi(\xi^2-1)}{r_n(\xi^2-\eta^2)} \left[\frac{\partial \psi_{jK}}{\partial r_n} \frac{\partial \psi_{iK'}}{\partial \xi} + \frac{\partial \psi_{jK}}{\partial \xi} \frac{\partial \psi_{iK'}}{\partial r_n} \right] \\
&- \frac{\eta(1-\eta^2)}{r_n(\xi^2-\eta^2)} \left[\frac{\partial \psi_{jK}}{\partial r_n} \frac{\partial \psi_{iK'}}{\partial \eta} + \frac{\partial \psi_{jK}}{\partial \eta} \frac{\partial \psi_{iK'}}{\partial r_n} \right] + \frac{1}{r_n^2} \left[\frac{\xi^2 \eta^2}{(\xi^2-1)(1-\eta^2)} \right. \\
&+ \frac{1}{\tan^2 \theta_n} - \frac{2\xi\eta}{\sqrt{(\xi^2-1)(1-\eta^2)}} \frac{\cos \phi}{\tan \theta_n} \left. \right] \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \phi} - \frac{\sqrt{(\xi^2-1)(1-\eta^2)}}{r_n^2(\xi^2-\eta^2)} \\
&\cdot \frac{\sin \phi}{\tan \theta_n} \cdot \left[\eta \cdot \left(\frac{\partial \psi_{jK}}{\partial \xi} \frac{\partial \psi_{iK'}}{\partial \phi} + \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \xi} \right) - \xi \left(\frac{\partial \psi_{jK}}{\partial \eta} \frac{\partial \psi_{iK'}}{\partial \phi} \right. \right. \\
&\left. \left. + \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \eta} \right) \right] \} . \quad (2.124)
\end{aligned}$$

$$\text{It is seen that } g_{jK,iK'} = g_{jK,iK'}(r_n, \theta_n). \quad (2.125)$$

To facilitate the reduction of the coupled differential equations, one sets

$$g_{jK,iK'}(r_n, \theta_n) = g_{jK,iK'}^{(1)}(r_n) - \cot \theta_n g_{jK,iK'}^{(2)}(r_n) + \cot^2 \theta_n g_{jK,iK'}^{(3)}(r_n), \quad (2.126)$$

where

$$g_{jK,iK'}^{(1)}(r_n) = \int_{R_\mu} d^3 R_\mu \left\{ \frac{\partial \psi_{jK}}{\partial r_n} \frac{\partial \psi_{iK'}}{\partial r_n} + \frac{\xi^2 + \eta^2 - 1}{r_n^2 (\xi^2 - \eta^2)} \left[(\xi^2 - 1) \cdot \frac{\partial \psi_{jK}}{\partial \xi} \frac{\partial \psi_{iK'}}{\partial \xi} + (1 - \eta^2) \frac{\partial \psi_{jK}}{\partial \eta} \frac{\partial \psi_{iK'}}{\partial \eta} \right] - \frac{\xi(\xi^2 - 1)}{r_n (\xi^2 - \eta^2)} \left[\frac{\partial \psi_{jK}}{\partial r_n} \frac{\partial \psi_{iK'}}{\partial \xi} + \frac{\partial \psi_{jK}}{\partial \xi} \frac{\partial \psi_{iK'}}{\partial r_n} \right] - \frac{\eta(1 - \eta^2)}{r_n (\xi^2 - \eta^2)} \left[\frac{\partial \psi_{jK}}{\partial r_n} \frac{\partial \psi_{iK'}}{\partial \eta} + \frac{\partial \psi_{jK}}{\partial \eta} \frac{\partial \psi_{iK'}}{\partial r_n} \right] + \frac{\xi^2 \eta^2}{r_n^2 (\xi^2 - 1)(1 - \eta^2)} \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \phi} \right\}, \quad (2.127)$$

$$g_{jK,iK'}^{(2)}(r_n) = \int_{R_\mu} d^3 R_\mu \left\{ \frac{2\xi\eta \cos \phi}{r_n^2 \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \phi} + \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{r_n^2 (\xi^2 - \eta^2)} \sin \phi \cdot \left[\eta \cdot \left(\frac{\partial \psi_{jK}}{\partial \xi} \frac{\partial \psi_{iK'}}{\partial \phi} + \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \xi} \right) - \xi \cdot \left(\frac{\partial \psi_{jK}}{\partial \eta} \frac{\partial \psi_{iK'}}{\partial \phi} + \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \eta} \right) \right] \right\}, \quad (2.128)$$

and

$$g_{jK, iK'}^{(3)}(r_n) = \int_{R_\mu} d^3 R_\mu \cdot \frac{1}{r_n^2} \frac{\partial \psi_{jK}}{\partial \phi} \frac{\partial \psi_{iK'}}{\partial \phi} \quad (2.129)$$

Carrying out the integration over ϕ , one obtains, for $\tau_\phi = c$,

$$g_{jK, iK'}^{(1)}(r_n) = 2\pi \{ g_{jK, iK'}^{(1,1)}(r_n) + K K' \cdot g_{jK, iK'}^{(1,2)}(r_n) \cdot (1-\delta_{K,0})(1-\delta_{K',0}) \} \delta_{K,K'} \quad (2.130)$$

where

$$\begin{aligned} g_{jK, iK'}^{(1,1)}(r_n) = & \frac{r_n^3}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta \cdot (\xi^2 - \eta^2) \cdot \left\{ \frac{\partial F_{jK}}{\partial r_n} \frac{\partial F_{iK'}}{\partial r_n} \right. \\ & + \frac{\xi^2 + \eta^2 - 1}{r_n^2 \cdot (\xi^2 - \eta^2)} \cdot \left[(\xi^2 - 1) \frac{\partial F_{jK}}{\partial \xi} \frac{\partial F_{iK'}}{\partial \xi} + (1 - \eta^2) \frac{\partial F_{jK}}{\partial \eta} \frac{\partial F_{iK'}}{\partial \eta} \right] \\ & - \frac{\xi(\xi^2 - 1)}{r_n \cdot (\xi^2 - \eta^2)} \cdot \left[\frac{\partial F_{jK}}{\partial r_n} \frac{\partial F_{iK'}}{\partial \xi} + \frac{\partial F_{jK}}{\partial \xi} \frac{\partial F_{iK'}}{\partial r_n} \right] \\ & \left. - \frac{\eta(1 - \eta^2)}{r_n(\xi^2 - \eta^2)} \cdot \left[\frac{\partial F_{jK}}{\partial r_n} \frac{\partial F_{iK'}}{\partial \eta} + \frac{\partial F_{jK}}{\partial \eta} \frac{\partial F_{iK'}}{\partial r_n} \right] \right\} \quad (2.131) \end{aligned}$$

and

$$g_{jK, iK'}^{(1,2)}(r_n) = \frac{r_n}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta \frac{(\xi^2 - \eta^2) \xi^2 \eta^2}{(\xi^2 - 1)(1 - \eta^2)} F_{jK} F_{iK'} \quad (2.132)$$

Also,

$$\begin{aligned}
 g_{jK, iK'}^{(2)}(r_n) = & \pi \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K',0}) + (1 - \delta_{K,0})(1 - \delta_{K',0})] \\
 & \cdot \{KK' g_{jK, iK'}^{(2,1)}(r_n) \cdot (\delta_{K, K'-1} + \delta_{K, K'+1}) \\
 & - [K' g_{jK, iK'}^{(2,2)}(r_n) - K g_{jK, iK'}^{(2,3)}(r_n)] (\delta_{K, K'-1} - \delta_{K, K'+1})\},
 \end{aligned} \tag{2.133}$$

where

$$g_{jK, iK'}^{(2,1)}(r_n) = \frac{r_n}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta \frac{2(\xi^2 - \eta^2) \cdot \xi \cdot \eta}{\sqrt{(\xi^2 - 1)(1 - \eta^2)}} F_{jK} F_{iK'}, \tag{2.134}$$

$$\begin{aligned}
 g_{jK, iK'}^{(2,2)}(r_n) = & \frac{r_n}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta \sqrt{(\xi^2 - 1)(1 - \eta^2)} \\
 & \cdot \left[\eta \frac{\partial F_{jK}}{\partial \xi} F_{iK'} - \xi \frac{\partial F_{jK}}{\partial \eta} F_{iK'} \right],
 \end{aligned} \tag{2.135}$$

and

$$\begin{aligned}
 g_{jK, iK'}^{(2,3)}(r_n) = & \frac{r_n}{8} \int_1^{\infty} d\xi \int_{-1}^1 d\eta \sqrt{(\xi^2 - 1)(1 - \eta^2)} \\
 & \cdot \left[\eta F_{jK} \frac{\partial F_{iK'}}{\partial \xi} - \xi F_{jK} \frac{\partial F_{iK'}}{\partial \eta} \right].
 \end{aligned} \tag{2.136}$$

One notes from the definitions (Equations 2.116 and 2.117) that

$$g_{jK, iK'}^{(2,1)}(r_n) = \frac{2 \mathfrak{J}_{jK, iK'}^{(2)}(r_n)}{r_n^2}, \quad (2.137)$$

$$g_{jK, iK'}^{(2,2)}(r_n) = \frac{\mathfrak{J}_{iK', jK}^{(1)}(r_n)}{r_n^2}, \quad (2.138)$$

and

$$g_{jK, iK'}^{(2,3)}(r_n) = \frac{\mathfrak{J}_{jK, iK'}^{(1)}(r_n)}{r_n^2}. \quad (2.139)$$

These three relations are used in Equation (2.178) below to further reduce the expression for $g_{jK, iK'}^{(2)}(r_n)$.

The third term in $g_{jK, iK'}(r_n, \theta_n)$, Equation (2.129), becomes

$$g_{jK, iK'}^{(3)}(r_n) = 2\pi K K' g_{jK, iK'}^{(3,1)}(r_n) \cdot \delta_{K, K'}, \quad (2.140)$$

where

$$g_{jK, iK'}^{(3,1)}(r_n) = \frac{r_n}{8} \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta (\xi^2 - \eta^2) F_{jK} F_{iK'}. \quad (2.141)$$

It is shown in Appendix B by use of the orthonormality properties of the electronic wave functions, that

$$\frac{\pi}{4} r_n^3 \int_{\xi=1}^{\infty} d\xi \int_{\eta=-1}^1 d\eta (\xi^2 - \eta^2) F_{jK} F_{iK} = \delta_{j,i}. \quad (B.9)$$

Thus, one obtains

$$g_{jK,iK}^{(3,1)}(r_n) = \frac{1}{2\pi r_n^2} \delta_{j,i} \quad (2.142)$$

and

$$g_{jK,iK'}^{(3)}(r_n) = \frac{KK'}{r_n^2} \delta_{j,i} \delta_{K,K'} \quad (2.143)$$

In a similar manner, the integration over ϕ yields, for $\tau_\phi = s$,

$$g_{jK,iK'}^{(1)}(r_n) = 2\pi \{ g_{jK,iK'}^{(1,1)}(r_n) + KK' \cdot g_{jK,iK'}^{(1,2)}(r_n) \} \\ \cdot (1-\delta_{K,0})(1-\delta_{K',0}) \delta_{K,K'} \quad (2.144)$$

where $g_{jK,iK'}^{(1,1)}(r_n)$ and $g_{jK,iK'}^{(1,2)}(r_n)$ have been defined above (Equations 2.131 and 2.132). Also,

$$g_{jK,iK'}^{(2)}(r_n) = \pi (1-\delta_{K,0}) \cdot (1-\delta_{K',0}) \cdot \{ KK' \cdot g_{jK,iK'}^{(2,1)}(r_n) \\ \cdot (\delta_{K,K'-1} + \delta_{K,K'+1}) + (K' g_{jK,iK'}^{(2,2)}(r_n) + K g_{jK,iK'}^{(2,3)}(r_n)) \\ \cdot (\delta_{K,K'-1} - \delta_{K,K'+1}) \} \quad (2.145)$$

where $g_{jK,iK'}^{(2,1)}(r_n)$, $g_{jK,iK'}^{(2,2)}(r_n)$, and $g_{jK,iK'}^{(2,3)}(r_n)$ have been defined in Equations (2.134), (2.135), and (2.136). The result for the third term is identical to that for $\tau_\phi = c$:

$$g_{jK, iK'}^{(3)}(r_n) = 2\pi \, KK' \cdot g_{jK, iK'}^{(3,1)}(r_n) \cdot \delta_{K, K'} \quad , \quad (2.140)$$

where

$$g_{jK, iK}^{(3,1)}(r_n) = \frac{1}{2\pi r_n} \delta_{j, i} \quad . \quad (2.142)$$

Thus,

$$g_{jK, iK'}^{(3)}(r_n) = \frac{KK'}{r_n} \delta_{j, i} \delta_{K, K'} \quad . \quad (2.143)$$

XI. SYMMETRY OF COUPLING PARAMETERS WITH RESPECT TO INTERCHANGE OF THE ELECTRONIC STATE INDICES jK AND iK

One recalls that $\mathcal{R}_{jK, iK'}(r_n)$ is proportional to $\delta_{K, K'}$ (Equations 2.108 and 2.111). Considering then

$$\begin{aligned} \mathcal{R}_{jK, iK}^{(1)}(r_n) &= \frac{r_n^3}{8} \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) F_{jK} \frac{\partial F_{iK}}{\partial r_n} \\ &\quad - \frac{r_n^2}{8} \int_1^\infty d\xi \int_{-1}^1 d\eta \left\{ \xi(\xi^2 - 1) F_{jK} \frac{\partial F_{iK}}{\partial \xi} + \eta(1 - \eta^2) F_{jK} \frac{\partial F_{iK}}{\partial \eta} \right\} \quad , \end{aligned} \quad (2.109)$$

one notes first that

$$\delta_{ji} = \frac{\pi r_n^3}{4} \int_1^\infty d\xi \int_1^1 d\eta (\xi^2 - \eta^2) F_{jK} F_{iK} \quad . \quad (B.9)$$

Operating on the latter with $\frac{\partial}{\partial r_n}$ yields

$$0 = \frac{\pi}{4} \left\{ 3r_n^2 \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) F_{jK} F_{iK} \right. \\ \left. + r_n^3 \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) \left[F_{jK} \frac{\partial F_{iK}}{\partial r_n} + \frac{\partial F_{jK}}{\partial r_n} F_{iK} \right] \right\} ;$$

thus,

$$\int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) F_{jK} \frac{\partial F_{iK}}{\partial r_n} = - \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) F_{iK} \frac{\partial F_{jK}}{\partial r_n} \\ - \frac{3}{r_n} \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) F_{iK} F_{jK} . \quad (2.146)$$

Integration by parts yields

$$\int_1^\infty d\xi \int_{-1}^1 d\eta \xi (\xi^2 - 1) F_{jK} \frac{\partial F_{iK}}{\partial \xi} = - \int_1^\infty d\xi \int_{-1}^1 d\eta \cdot \left\{ \xi (\xi^2 - 1) F_{iK} \frac{\partial F_{jK}}{\partial \xi} \right. \\ \left. + (3\xi^2 - 1) F_{iK} F_{jK} \right\} , \quad (2.147)$$

in which it is assumed that $\lim_{\xi \rightarrow \infty} [\xi (\xi^2 - 1) F_{iK} F_{jK}] = 0$, and

$$\int_1^\infty d\xi \int_{-1}^1 d\eta \eta (1 - \eta^2) F_{jK} \frac{\partial F_{iK}}{\partial \eta} = - \int_1^\infty d\xi \int_{-1}^1 d\eta \cdot \left\{ \eta (1 - \eta^2) F_{iK} \frac{\partial F_{jK}}{\partial \eta} \right. \\ \left. + (1 - 3\eta^2) F_{iK} F_{jK} \right\} . \quad (2.148)$$

One obtains from Equations (2.147) and (2.148)

$$\begin{aligned}
& \int_1^\infty d\xi \int_{-1}^1 d\eta \left\{ \xi(\xi^2-1) F_{jK} \frac{\partial F_{iK}}{\partial \xi} + \eta(1-\eta^2) F_{jK} \frac{\partial F_{jK}}{\partial \eta} \right\} \\
& = - \int_1^\infty d\xi \int_{-1}^1 d\eta \left\{ \xi(\xi^2-1) F_{iK} \frac{\partial F_{jK}}{\partial \xi} + \eta(1-\eta^2) F_{iK} \frac{\partial F_{jK}}{\partial \eta} \right\} \\
& - 3 \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2-\eta^2) F_{iK} F_{jK} .
\end{aligned} \tag{2.149}$$

Substitution of Equations (2.146) and (2.149) in Equation (2.109)

yields

$$\begin{aligned}
Q_{jK,iK}^{(1)}(r_n) & = - \frac{r_n^3}{8} \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2-\eta^2) F_{iK} \frac{\partial F_{jK}}{\partial r_n} \\
& + \frac{r_n^2}{8} \int_1^\infty d\xi \int_{-1}^1 d\eta \left\{ \xi(\xi^2-1) \cdot F_{iK} \frac{\partial F_{jK}}{\partial \xi} + \eta(1-\eta^2) F_{iK} \frac{\partial F_{jK}}{\partial \eta} \right\} .
\end{aligned} \tag{2.150}$$

Comparison of Equations (2.150) and (2.109) reveals that

$$Q_{jK,iK}^{(1)}(r_n) = -Q_{iK,jK}^{(1)}(r_n) ; \tag{2.151}$$

i.e., this coupling parameter is antisymmetric in the electronic state indices j and i . Letting $i=j$ yields

$$Q_{jK,jK}^{(1)}(r_n) = -Q_{jK,jK}^{(1)}(r_n) ;$$

therefore, the diagonal element of this parameter is identically zero,

$$\mathcal{Q}_{jK,jK}^{(1)}(r_n) = 0 \quad . \quad (2.152)$$

Thus, there is no diagonal coupling through the term $\mathcal{Q}_{jK,jK}^{(1)}(r_n)$.

One recalls from Equation (2.115) that $\mathcal{J}_{jK,iK'}(r_n)$ is proportional to $\delta_{K,K'+1}$. One has

$$\begin{aligned} \mathcal{J}_{jK,iK'}^{(1)}(r_n) &= \frac{r_n^3}{8} \cdot \int_1^\infty d\xi \int_{-1}^1 d\eta \sqrt{(\xi^2-1)(1-\eta^2)} \cdot \left[\eta F_{jK} \frac{\partial F_{iK'}}{\partial \xi} \right. \\ &\quad \left. - \xi \frac{\partial F_{iK'}}{\partial \eta} \right] \quad . \end{aligned} \quad (2.116)$$

Integration by parts yields

$$\begin{aligned} \mathcal{J}_{jK,iK'}^{(1)}(r_n) &= \frac{r_n^3}{8} \cdot \int_1^\infty d\xi \int_{-1}^1 d\eta \left\{ -\eta \sqrt{(\xi^2-1)(1-\eta^2)} F_{iK'} \frac{\partial F_{jK}}{\partial \xi} \right. \\ &\quad - \xi \eta \frac{\sqrt{1-\xi^2}}{\sqrt{\xi^2-1}} F_{iK'} F_{jK} + \xi \sqrt{(\xi^2-1)(1-\eta^2)} F_{iK'} \frac{\partial F_{jK}}{\partial \eta} \\ &\quad \left. - \xi \eta \frac{\sqrt{\xi^2-1}}{\sqrt{1-\eta^2}} F_{iK'} F_{jK} \right\} \quad , \end{aligned}$$

where it is assumed that $\lim_{\xi \rightarrow \infty} [\sqrt{\xi^2-1} F_{jK} F_{iK'}] = 0$. Reordering the terms

one has

$$\begin{aligned} \mathcal{J}_{jK, iK'}^{(1)}(r_n) = & -\frac{r_n^3}{8} \int_1^\infty d\xi \int_{-1}^1 d\eta \sqrt{(\xi^2-1)(1-\eta^2)} \left[\eta F_{iK'} \frac{\partial F_{jK}}{\partial \xi} \right. \\ & \left. - \xi F_{iK'} \frac{\partial F_{jK}}{\partial \eta} \right] - \frac{r_n^3}{8} \int_1^\infty d\xi \int_{-1}^1 d\eta \frac{(\xi^2-\eta^2)\xi\eta}{\sqrt{(\xi^2-1)(1-\eta^2)}} F_{iK'} F_{jK}. \end{aligned} \quad (2.153)$$

Referring to Equations (2.116) and (2.117), one has

$$\mathcal{J}_{jK, iK'}^{(1)}(r_n) = -\mathcal{J}_{iK', jK}^{(1)}(r_n) - \mathcal{J}_{iK', jK}^{(2)}(r_n). \quad (2.154)$$

From the definition given in Equation (2.117), one has

$$\mathcal{J}_{jK, iK'}^{(2)}(r_n) = \mathcal{J}_{iK', jK}^{(2)}(r_n). \quad (2.155)$$

For $K' = K+1$, one obtains from Equation (2.115)

$$\begin{aligned} \mathcal{J}_{jK, iK'}(r_n) \cdot \delta_{K, K'-1} = & \alpha_{K, K'} \cdot \{ \mathcal{J}_{jK, iK'}^{(1)}(r_n) + K' \mathcal{J}_{jK, iK'}^{(2)}(r_n) \} \\ & \cdot \delta_{K, K'-1}, \end{aligned} \quad (2.156)$$

where

$$\alpha_{K, K'} = \pi \cdot [\sqrt{2} (\delta_{K, 0} + \delta_{K', 0}) + (1-\delta_{K, 0})(1-\delta_{K', 0})] \quad (2.157)$$

Substitution of Equation (2.154) in Equation (2.156) yields

$$\begin{aligned} \mathcal{J}_{jK, iK'}(r_n) \cdot \delta_{K, K'-1} = & -\alpha_{K, K'} \cdot \{ \mathcal{J}_{iK', jK}^{(1)}(r_n) - (K'-1) \\ & \mathcal{J}_{iK', jK}^{(2)}(r_n) \} \delta_{K, K'-1}. \end{aligned} \quad (2.158)$$

One notes that $K = K' - 1$ is equivalent to $K + 1 = K'$; so that

$$\begin{aligned} \mathcal{J}_{jK, iK'}(r_n) \delta_{K, K'-1} = & -\alpha_{K, K'} \{ \mathcal{J}_{iK', jK}^{(1)}(r_n) - K \mathcal{J}_{iK', jK}^{(2)}(r_n) \} \\ & \cdot \delta_{K', K+1} \end{aligned} \quad (2.159)$$

Referring to Equation (2.115) for $K' = K - 1$, one has

$$\begin{aligned} \mathcal{J}_{jK, iK'}(r_n) \delta_{K, K'+1} = & \alpha_{K, K'} \{ \mathcal{J}_{jK, iK'}^{(1)}(r_n) - K' \mathcal{J}_{jK, iK'}^{(2)}(r_n) \} \\ & \cdot \delta_{K, K'+1} \end{aligned} \quad (2.160)$$

If one now relabels the last expression, letting $j \rightarrow i$, $i \rightarrow j$, $K' \rightarrow K$, and $K \rightarrow K'$, one has

$$\begin{aligned} \mathcal{J}_{iK', jK}(r_n) \cdot \delta_{K', K+1} = & \alpha_{K', K} \{ \mathcal{J}_{iK', jK}^{(1)}(r_n) - K \mathcal{J}_{iK', jK}^{(2)}(r_n) \} \\ & \cdot \delta_{K', K+1} \end{aligned} \quad (2.161)$$

From Equations (2.159) and (2.161), one has found

$$\mathcal{J}_{jK, iK'}(r_n) \delta_{K, K'+1} = -\mathcal{J}_{iK', jK}(r_n) \delta_{K', K+1} \quad (2.162)$$

since $\alpha_{K', K} = \alpha_{K, K'}$. Thus $\mathcal{J}_{jK, iK'}(r_n)$ is antisymmetric in the indices jK and iK' under the selection rules imposed on K and K' .

From the definition of $g_{jK, iK'}(r_n, \theta_n)$ as

$$g_{jK, iK'}(r_n, \theta_n) = \int_{R_\mu} (\vec{\nabla}_n \psi_{jK}) \cdot (\vec{\nabla} \psi_{iK'}) d^3 R_\mu \quad (2.68)$$

it is seen that (Equation 2.125)

$$g_{iK',jK}(r_n, \theta_n) = g_{jK,iK'}(r_n, \theta_n) \quad ; \quad (2.163)$$

i.e., this coupling parameter is symmetric in the indices jK and iK' .

Its component $g_{jK,iK'}^{(1)}(r_n)$ is also seen from Equation (2.127) to be symmetric in the indices jK and iK' :

$$g_{iK',jK}^{(1)}(r_n) = g_{jK,iK'}^{(1)}(r_n) \quad . \quad (2.164)$$

It is seen from Equations (2.131) and (2.132) that the components of $g_{jK,iK'}^{(1)}(r_n)$ are symmetric in the indices jK and iK' :

$$g_{jK,iK'}^{(1,1)}(r_n) = g_{iK',jK}^{(1,1)}(r_n) \quad (2.165)$$

and

$$g_{jK,iK'}^{(1,2)}(r_n) = g_{iK',jK}^{(1,2)}(r_n) \quad . \quad (2.166)$$

The definition of $g_{jK,iK'}^{(2)}(r_n)$ (Equation 2.128) reveals that

$$g_{jK,iK'}^{(2)}(r_n) = g_{iK',jK}^{(2)}(r_n) \quad . \quad (2.167)$$

The component $g_{jK,iK'}^{(2,1)}(r_n)$ is seen from Equation (2.134) to be symmetric in the indices jK and iK' :

$$g_{jK, iK'}^{(2,1)}(r_n) = g_{iK', jK}^{(2,1)}(r_n) \quad (2.168)$$

The other two components of $g_{jK, iK'}^{(2)}(r_n)$ do not have a definite symmetry with respect to the indices jK and iK' ; however, it is seen from Equations (2.135) and (2.136) that

$$g_{iK', jK}^{(2,2)}(r_n) = g_{jK, iK'}^{(2,3)}(r_n) \quad (2.169)$$

and

$$g_{iK', jK}^{(2,3)}(r_n) = g_{jK, iK'}^{(2,2)}(r_n) \quad (2.170)$$

Thus, the term given by Equation (2.138) for $K'=K+1$,

$$\begin{aligned} g_{jK, iK'}^{(2)}(r_n) \cdot \delta_{K, K'-1} &= \alpha_{K, K'} \cdot \{ K K' g_{jK, iK'}^{(2,1)}(r_n) \\ &- K' g_{jK, iK'}^{(2,2)}(r_n) + K g_{jK, iK'}^{(2,3)}(r_n) \} \cdot \delta_{K, K'-1} \quad (2.171) \end{aligned}$$

becomes, using the above results (Equations 2.168, 2.169, and 2.170),

$$\begin{aligned} g_{jK, iK'}^{(2)}(r_n) \cdot \delta_{K, K'-1} &= \alpha_{K, K'} \cdot \{ K' K g_{iK', jK}^{(2,1)}(r_n) \\ &- K' g_{iK', jK}^{(2,3)}(r_n) + K g_{iK', jK}^{(2,2)}(r_n) \} \cdot \delta_{K', K-1} \quad (2.172) \end{aligned}$$

Again one notes that $\delta_{K, K'-1} = \delta_{K', K+1}$ and reorders terms:

$$g_{jK, iK'}^{(2)}(r_n) \cdot \delta_{K, K'-1} = \alpha_{K, K'} \cdot \{ K' K g_{iK', jK}^{(2,1)}(r_n)$$

$$+ K g_{iK',jK}^{(2,2)}(r_n) - K' g_{iK',jK}^{(2,3)}(r_n) \} \cdot \delta_{K',K+1}. \quad (2.173)$$

The term given by Equation (2.133) for $K'=K-1$ is

$$g_{jK,iK'}^{(2)}(r_n) \cdot \delta_{K,K'+1} = \alpha_{K,K'} \cdot \{ K K' g_{jK,iK'}^{(2,1)}(r_n) \\ + K' g_{jK,iK'}^{(2,2)}(r_n) - K g_{jK,iK'}^{(2,3)}(r_n) \} \cdot \delta_{K,K'+1}. \quad (2.174)$$

If one relabels the above expression, letting $j \rightarrow i$, $i \rightarrow j$, $K \rightarrow K'$, and $K' \rightarrow K$, one obtains

$$g_{iK',jK}^{(2)}(r_n) \delta_{K',K+1} = \alpha_{K',K} \cdot \{ K' K g_{iK',jK}^{(2,1)}(r_n) \\ + K g_{iK',jK}^{(2,2)}(r_n) - K' g_{iK',jK}^{(2,3)}(r_n) \} \delta_{K',K+1}. \quad (2.175)$$

Thus, using Equation (2.173) and $\alpha_{K',K} = \alpha_{K,K'}$, one has

$$g_{jK,iK'}^{(2)}(r_n) \cdot \delta_{K,K'-1} = g_{iK',jK}^{(2)}(r_n) \cdot \delta_{K',K+1}; \quad (2.176)$$

and the symmetry of $g_{jK,iK'}^{(2)}(r_n)$ to transposition of the indices jK and iK' is seen to be valid under the selection rules on K and K' , despite the lack of this symmetry in $g_{jK,iK'}^{(2,2)}(r_n)$ and $g_{jK,iK'}^{(2,3)}(r_n)$.

One recalls that $g_{jK,iK'}^{(2)}(r_n)$ may be expressed in terms of the components of $\mathcal{J}_{jK,iK'}(r_n)$. One has from Equation (2.133), letting

$$\alpha_{K,K'} = \Pi \cdot [\sqrt{2} (\delta_{K,0} + \delta_{K',0}) + (1 - \delta_{K,0})(1 - \delta_{K',0})],$$

$$\begin{aligned}
g_{jK, iK'}^{(2)}(r_n) = & \alpha_{K, K'} \{ KK' g_{jK, iK'}^{(2,1)}(r_n) \cdot (\delta_{K, K'-1} \\
& + \delta_{K, K'+1}) - [K' g_{jK, iK'}^{(2,2)}(r_n) - K g_{jK, iK'}^{(2,3)}(r_n)] \\
& \cdot (\delta_{K, K'-1} - \delta_{K, K'+1}) \} .
\end{aligned} \tag{2.177}$$

Substitutions of Equations (2.137), (2.138), and (2.139) yields

$$\begin{aligned}
g_{jK, iK'}^{(2)}(r_n) = & \frac{\alpha_{K, K'}}{r_n^2} \{ 2KK' \mathcal{J}_{jK, iK'}^{(2)}(r_n) \cdot (\delta_{K, K'-1} \\
& + \delta_{K, K'+1}) - [K' \mathcal{J}_{iK', jK}^{(1)}(r_n) - K \mathcal{J}_{jK, iK'}^{(1)}(r_n)] \cdot \\
& \cdot (\delta_{K, K'-1} - \delta_{K, K'+1}) \} .
\end{aligned} \tag{2.178}$$

The symmetry relationships in Equations (2.154) and (2.155) yield the result

$$\begin{aligned}
g_{jK, iK'}^{(2)}(r_n) = & \frac{\alpha_{K, K'}}{r_n^2} \cdot \{ 2KK' \mathcal{J}_{jK, iK'}^{(2)}(r_n) \cdot (\delta_{K, K'-1} \\
& + \delta_{K, K'+1}) + [K' (\mathcal{J}_{jK, iK'}^{(1)}(r_n) + \mathcal{J}_{jK, iK'}^{(2)}(r_n) \\
& + K \mathcal{J}_{jK, iK'}^{(1)}(r_n))] \cdot (\delta_{K, K'-1} - \delta_{K, K'+1}) \} ,
\end{aligned}$$

or one can collect terms to obtain

$$g_{jK, iK'}^{(2)}(r_n) = \frac{\alpha_{K, K'}}{r_n^2} \cdot \{ 2KK' \mathcal{J}_{jK, iK'}^{(2)}(r_n) \cdot (\delta_{K, K'-1}$$

$$+ \delta_{K, K'+1}) + [(K'+K) \cdot \mathcal{J}_{jK, iK'}^{(1)}(r_n) + K' \cdot \mathcal{J}_{jK, iK'}^{(2)}(r_n)] \\ \cdot (\delta_{K, K'-1} - \delta_{K, K'+1}) \} .$$

Grouping the multipliers of a given δ -function, one has

$$g_{jK, iK'}^{(2)}(r_n) = \frac{\alpha_{K, K'}}{r_n^2} \cdot \{ [(K'+K) \cdot \mathcal{J}_{jK, iK'}^{(1)}(r_n) + K'(2K+1) \\ \cdot \mathcal{J}_{jK, iK'}^{(2)}(r_n)] \delta_{K, K'-1} - [(K'+K) \cdot \mathcal{J}_{jK, iK'}^{(1)}(r_n) \\ - K'(2K-1) \cdot \mathcal{J}_{jK, iK'}^{(2)}(r_n)] \delta_{K, K'+1} \} .$$

The last result can be expressed as

$$g_{jK, iK'}^{(2)}(r_n) = \frac{\alpha_{K, K'}}{r_n^2} \cdot \{ (2K+1) \cdot [\mathcal{J}_{jK, iK'}^{(1)}(r_n) + K' \mathcal{J}_{jK, iK'}^{(2)}(r_n)] \\ \cdot \delta_{K, K'-1} - (2K-1) \cdot [\mathcal{J}_{jK, iK'}^{(1)}(r_n) - K' \mathcal{J}_{jK, iK'}^{(2)}(r_n)] \\ \cdot \delta_{K, K'+1} \} , \quad (2.179)$$

which is identical to

$$g_{jK, iK'}^{(2)}(r_n) = (2K+1) \frac{\mathcal{J}_{jK, iK'}(r_n)}{r_n^2} \delta_{K, K'-1} - (2K-1) \frac{\mathcal{J}_{jK, iK'}(r_n)}{r_n^2} \\ \cdot \delta_{K, K'+1} , \quad (2.180)$$

as may be seen from Equation (2.115). One may shorten the above expression by writing

$$g_{jK, iK'}^{(2)}(r_n) = \pi \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K',0}) + (1 - \delta_{K,0})(1 - \delta_{K',0})] \cdot \left\{ \pm \frac{2K \pm 1}{r_n} [\mathcal{J}_{jK, iK'}^{(1)}(r_n) \pm K' \mathcal{J}_{jK, iK'}^{(2)}(r_n)] \right\}, \quad (2.181)$$

where the upper signs correspond to $K'=K+1$ and the lower signs correspond to $K'=K-1$.

From the definition given in Equation (2.129), it is seen that

$$g_{jK, iK'}^{(3)}(r_n) = g_{iK', jK}^{(3)}(r_n), \quad (2.182)$$

symmetric in the indices jK and iK' . From the definition (Equation 2.141), it is seen that $g_{jK, iK'}^{(3,1)}(r_n)$ is also symmetric in the indices jK and iK' :

$$g_{jK, iK'}^{(3,1)}(r_n) = g_{iK', jK}^{(3,1)}(r_n). \quad (2.183)$$

This term contributes only to the diagonal coupling in the basis chosen here, so that its symmetry is not used in the following.

XII. FURTHER REDUCTION OF THE COUPLED EQUATIONS

Having obtained the form and angular dependence of the coupling parameters, one continues the reduction of Equation (2.77), which is written as

$$\begin{aligned}
& \frac{1}{r_n} A_{LK} \left\{ p_L^K \left[\frac{d^2 \phi_j^{LK}}{dr_n^2} - \frac{(V_j^K - E)}{\epsilon} \phi_j^{LK} \right] + \frac{1}{r_n^2} \left(\frac{d^2 p_L^K}{d\theta_n^2} + \frac{1}{\tan \theta_n} \right. \right. \\
& \quad \left. \left. \cdot \frac{dp_L^K}{d\theta_n} \right) \phi_j^{LK} \right\} + \frac{1}{r_n} \sum_{K'} A_{LK'} \left\{ p_L^{K'} \sum_i \left[2 \mathcal{Q}_{jK,iK'} \frac{d\phi_i^{LK'}}{dr_n} \right. \right. \\
& \quad \left. \left. + \frac{\partial \mathcal{Q}_{jK,iK'}}{\partial r_n} \phi_i^{LK'} + \frac{1}{r_n^2} \frac{\partial \mathcal{J}_{jK,iK'}}{\partial \theta_n} \phi_i^{LK'} + \frac{\mathcal{J}_{jK,iK'}}{r_n^2 \tan \theta_n} \phi_i^{LK'} \right. \right. \\
& \quad \left. \left. - g_{jK,iK'} \phi_i^{LK'} \right] + \frac{1}{r_n^2} \frac{dp_L^{K'}}{d\theta_n} \sum_i 2 \mathcal{J}_{jK,iK'} \phi_i^{LK'} \right\} = 0 \quad (2.184)
\end{aligned}$$

One notes that the associated Legendre functions obey the equation

$$\frac{d^2 p_L^K}{d\theta_n^2} + \frac{1}{\tan \theta_n} \frac{dp_L^K}{d\theta_n} = \left\{ -L(L+1) + \frac{K^2}{\sin^2 \theta_n} \right\} p_L^K, \quad (2.185)$$

that

$$\frac{\partial \mathcal{J}_{jK,iK'}}{\partial \theta_n} = 0, \quad (2.119)$$

and that

$$\begin{aligned}
g_{jK,iK'}(r_n, \theta_n) &= g_{jK,iK'}^{(1)}(r_n) - g_{jK,iK'}^{(2)}(r_n) \cot \theta_n \\
&+ g_{jK,iK'}^{(3)}(r_n) \cot^2 \theta_n. \quad (2.126)
\end{aligned}$$

One obtains, canceling the common factor $\frac{1}{r_n}$,

$$\begin{aligned}
& A_{LK} P_L^K \left[\frac{d^2 \phi_j^{L,K}}{dr_n^2} - \left(\frac{V_j^{K-E}}{\epsilon} + \frac{L(L+1)}{r_n^2} - \frac{K^2}{r_n^2 \sin^2 \theta_n} \right) \phi_j^{L,K} \right] \\
& + \sum_{K'} A_{LK'} \left\{ P_L^{K'} \sum_i \left[2 \mathcal{Q}_{jK,iK'} \frac{d\phi_i^{LK'}}{dr_n} - \left(g_{jK,iK'}^{(1)} \right. \right. \right. \\
& - g_{jK,iK'}^{(2)} \cot \theta_n + g_{jK,iK'}^{(3)} \cot^2 \theta_n - \frac{d\mathcal{Q}_{jK,iK'}}{dr_n} \\
& \left. \left. - \frac{\mathcal{J}_{jK,iK'}}{r_n^2} \cot \theta_n \right) \phi_i^{LK'} \right] + \frac{dP_L^{K'}}{d\theta_n} \sum_i \frac{2\mathcal{J}_{jK,iK'}}{r_n^2} \phi_i^{LK'} \right\} = 0. \quad (2.186)
\end{aligned}$$

In the following, one considers only the case $\tau_\phi = c$. Recalling that $\mathcal{Q}_{jK,iK'}(r_n)$, $g_{jK,iK'}^{(1)}(r_n)$, and $g_{jK,iK'}^{(3)}(r_n)$ are proportional to $\delta_{K,K'}$ and that $\mathcal{J}_{jK,iK'}(r_n)$ and $g_{jK,iK'}^{(2)}(r_n)$ are proportional to $\delta_{K',K\pm 1}$, one regroups the coupling terms of the preceeding equation:

$$\begin{aligned}
& A_{LK} \left\{ P_L^K \frac{d^2 \phi_j^{L,K}}{dr_n^2} - \left[\frac{V_j^{K-E}}{\epsilon} + \frac{L(L+1)}{r_n^2} - \frac{K^2}{r_n^2 \sin^2 \theta_n} \right] P_L^K \phi_j^{LK} \right\} \\
& = \sum_{K'} A_{LK'} \sum_i \left\{ \left[\left(g_{jK,iK'}^{(1)} - \frac{d\mathcal{Q}_{jK,iK'}}{dr_n} + g_{jK,iK'}^{(3)} \cot^2 \theta_n \right) \right. \right. \\
& \cdot P_L^{K'} \phi_i^{LK'} - 2 \mathcal{Q}_{jK,iK'} P_L^{K'} \frac{d\phi_i^{L,K'}}{dr_n} \left. \right] - \left[g_{jK,iK'}^{(2)} \cot \theta_n \right. \\
& \cdot P_L^{K'} + \frac{\mathcal{J}_{jK,iK'}}{r_n^2} \left(\cot \theta_n P_L^{K'} + 2 \frac{dP_L^{K'}}{d\theta_n} \right) \left. \right] \phi_i^{L,K'} \right\} = \sum_{K'} A_{LK'} \\
& \cdot \sum_i \left\{ 2\pi \left[\left(g_{jK,iK'}^{(1,1)} - \frac{d\mathcal{Q}_{jK,iK'}^{(1)}}{dr_n} + KK' \left\{ g_{jK,iK'}^{(1,2)} \right. \right. \right. \right.
\end{aligned}$$

$$\begin{aligned}
& + g_{jK,iK'}^{(3,1)} \cot^2 \theta_n \Bigg) p_L^{K'} \phi_i^{LK'} - 2 Q_{jK,iK'}^{(1)} p_L^{K'} \\
& \cdot \frac{d\phi_i^{L,K'}}{dr_n} \Bigg] \cdot \delta_{K,K'} - \Pi \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K',0}) + (1-\delta_{K,0})(1-\delta_{K',0})] \\
& \cdot \left[\left\{ {}^{KK'} g_{jK,iK'}^{(2,1)} - K' g_{jK,iK'}^{(2,2)} + K g_{jK,iK'}^{(2,3)} \right\} \right. \\
& \cdot \cot \theta_n p_L^{K'} + \frac{\{ \mathcal{J}_{jK,iK'}^{(1)} + K' \cdot \mathcal{J}_{jK,iK'}^{(2)} \}}{r_n^2} \cdot \left\{ \cot \theta_n p_L^{K'} \right. \\
& + 2 \frac{dp_L^{K'}}{d\theta_n} \Bigg) \delta_{K,K'-1} + \{ {}^{KK'} g_{jK,iK'}^{(2,1)} + K' g_{jK,iK'}^{(2,2)} \\
& - K g_{jK,iK'}^{(2,3)} \} \cot \theta_n p_L^{K'} + \frac{\{ \mathcal{J}_{jK,iK'}^{(1)} - K' \cdot \mathcal{J}_{jK,iK'}^{(2)} \}}{r_n^2} \\
& \cdot \left. \left\{ \cot \theta_n p_L^{K'} + 2 \frac{dp_L^{K'}}{d\theta_n} \right\} \delta_{K,K'+1} \right] \phi_i^{L,K'} \Bigg\}. \tag{2.187}
\end{aligned}$$

Multiplication of the preceeding equation by $p_L^K(\cos \theta_n)$ and integration over the θ_n volume element, $\sin \theta_n d\theta_n$, yields the following equation:

$$\begin{aligned}
A_{LK} \cdot \left\{ C_{LKK}^{(1)} \frac{d^2 \phi_j^{L,K}}{dr_n^2} - \left[\left(\frac{V_{jK-E}}{\epsilon} + \frac{L(L+1)}{r_n^2} \right) C_{LKK}^{(1)} - \frac{K^2}{r_n^2} C_{LKK}^{(2)} \right] \right. \\
\cdot \phi_j^{L,K} \Bigg\} = \sum_{K'=0}^L A_{LK'} \sum_i \left\{ 2\pi \left[\left\{ g_{jK,iK}^{(1,1)} - \frac{dQ_{jK,iK}}{dr_n} \right. \right. \right. \\
\left. \left. + K^2 g_{jK,iK}^{(1,2)} \right\} C_{LKK}^{(1)} + K^2 g_{jK,iK}^{(3,1)} C_{LKK}^{(3)} \right] \phi_i^{LK} \right.
\end{aligned}$$

$$\begin{aligned}
& - 2 Q_{jK,iK}^{(1)} \cdot C_{LKK}^{(1)} \frac{d\phi_i^{L,K}}{dr_n} \Big] \delta_{K,K'} - \pi \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K',0}) \\
& + (1 - \delta_{K,0})(1 - \delta_{K',0})] \cdot \left[\left\{ {}^{KK'} g_{jK,iK'}^{(2,1)} + {}^{K'} g_{jK,iK'}^{(2,2)} \right. \right. \\
& \left. \left. + {}^{K'} g_{jK,iK'}^{(2,3)} \right\} C_{LKK'}^{(4)} + \frac{\{ \mathcal{J}_{jK,iK'}^{(1)} + {}^{K'} \mathcal{J}_{jK,iK'}^{(2)} \}}{r_n^2} \right. \\
& \left. \cdot \{ C_{LKK'}^{(4)} + 2 C_{LKK'}^{(5)} \} \right] \phi_i^{L,K'} \Big\} , \quad (2.188)
\end{aligned}$$

where the upper signs correspond to $K'=K+1$, the lower signs correspond to $K'=K-1$,

$$\begin{aligned}
C_{LKK}^{(1)} &= \int_{\theta=0}^{\pi} p_L^K(\cos \theta_n) p_L^K(\cos \theta_n) \sin \theta_n d\theta_n \\
&= \int_{x=-1}^1 p_L^K(x) p_L^K(x) dx = \frac{2}{2L+1} \cdot \frac{(L+K)!}{(L-K)!} ,
\end{aligned}$$

$$\begin{aligned}
C_{LKK}^{(2)} &= \int_{\theta=0}^{\pi} \frac{p_L^K(\cos \theta_n) p_L^K(\cos \theta_n)}{\sin^2 \theta_n} \sin \theta_n d\theta_n \\
&= \int_{x=-1}^1 \frac{p_L^K(x) p_L^K(x)}{(1-x^2)} dx = \frac{(L+K)!}{K(L-K)!} , \quad K \neq 0 ,
\end{aligned}$$

$$\begin{aligned}
C_{LKK}^{(3)} &= \int_{\theta=0}^{\pi} p_L^K(\cos \theta_n) p_L^K(\cos \theta_n) \cot^2 \theta_n \sin \theta_n d\theta_n \\
&= \int_{x=-1}^1 p_L^K(x) \cdot p_L^K(x) \cdot \frac{x^2}{1-x^2} dx = \frac{2(L-K)+1}{(2L+1)K} \cdot \frac{(L+K)!}{(L-K)!} ,
\end{aligned}$$

$$\begin{aligned}
C_{L,K,K+1}^{(4)} &= \int_{\theta_n=0}^{\pi} P_L^K(\cos \theta_n) P_L^{K+1}(\cos \theta_n) \cot \theta_n \sin \theta_n d\theta_n \\
&= \int_{x=-1}^1 P_L^K(x) P_L^{K+1}(x) \cdot \frac{x}{(1-x^2)^{1/2}} dx = \frac{2}{2L+1} \cdot \frac{(L+K-\frac{1}{2}+\frac{1}{2})!}{(L-K-\frac{1}{2}+\frac{1}{2})!},
\end{aligned}$$

and

$$\begin{aligned}
C_{L,K,K+1}^{(5)} &= \int_{\theta_n=0}^{\pi} P_L^K(\cos \theta_n) \frac{d}{d\theta_n} P_L^{K+1}(\cos \theta_n) \sin \theta_n d\theta_n \\
&= \int_{x=-1}^1 P_L^K(x) \cdot \frac{dP_L^{K+1}(x)}{dx} \cdot (1-x^2)^{1/2} dx = \pm \frac{2(L+\frac{1}{2}+\frac{1}{2})}{2L+1} \cdot \frac{(L+K-\frac{1}{2}+\frac{1}{2})!}{(L-K-\frac{1}{2}+\frac{1}{2})!}.
\end{aligned}$$

Noting that

$$\frac{A_{L,K+1}}{A_{L,K}} = \left[\frac{\delta_{K+1,0} + \sqrt{2}(1-\delta_{K+1,0})}{\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})} \right] \cdot \left[\left(L-K+\frac{1}{2}+\frac{1}{2} \right) \left(L+K+\frac{1}{2}+\frac{1}{2} \right) \right]^{-\frac{1}{2}},$$

$$\frac{C_{LKK}^{(2)}}{C_{LKK}^{(1)}} = \frac{2L+1}{2K},$$

$$\frac{C_{LKK}^{(3)}}{C_{LKK}^{(1)}} = \frac{L-K+\frac{1}{2}}{K},$$

$$\frac{C_{L,K,K+1}^{(4)}}{C_{LKK}^{(1)}} = (L+K)^{\pm 1},$$

$$\frac{C_{L,K,K+1}^{(5)}}{C_{LKK}^{(1)}} = \pm (L+\frac{1}{2}+\frac{1}{2}) \cdot (L+K)^{\pm 1},$$

and

$$\frac{A_{L,K+1}}{A_{L,K}} \cdot \frac{C_{L,K,K+1}^{(4)}}{C_{L,K,K}^{(1)}} = \left[\frac{\delta_{K+1,0} + \sqrt{2}(1-\delta_{K+1,0})}{\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})} \right] \cdot \sqrt{\frac{L-K+\frac{1}{2}+\frac{1}{2}}{L+K+\frac{1}{2}+\frac{1}{2}}},$$

one obtains from Equation (2.188)

$$\begin{aligned} \frac{d^2 \phi_j^{L,K}}{dr_n^2} - \left\{ \frac{V_{jK} - E}{\epsilon} + \frac{L(L+1) - K(K+1)}{r_n^2} \right\} \phi_j^{L,K} &= 2\pi \cdot \delta_{K^-,K} \\ \sum_i \left\{ \left[g_{jK,iK}^{(1,1)} + K^2 g_{jK,iK}^{(1,2)} - \frac{dQ_{jK,iK}^{(1)}}{dr_n} + K \cdot \left(L - K + \frac{1}{2} \right) \right. \right. \\ &\cdot g_{jK,iK}^{(3,1)} \left. \right] \phi_i^{LK} - 2 Q_{jK,iK}^{(1)} \frac{d\phi_i^{L,K}}{dr_n} \left. \right\} - \pi \sum_{K=0}^L \delta_{K^-,K+1} \\ &\cdot \left[\frac{\delta_{K+1,0} + \sqrt{2}(1-\delta_{K+1,0})}{\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})} \right] \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K+1,0}) + (1-\delta_{K,0})(1-\delta_{K+1,0})] \\ &\cdot \sqrt{\frac{L-K+\frac{1}{2}+\frac{1}{2}}{L+K+\frac{1}{2}+\frac{1}{2}}} \cdot \sum_i \left\{ K \cdot (K+1) g_{jK,i,K+1}^{(2,1)} + (K+1) g_{j,K,i,K+1}^{(2,2)} \right. \\ &+ K \cdot g_{j,K,i,K+1}^{(2,3)} \\ &\left. + (2L+1) \cdot \frac{[J_{j,K,i,K+1}^{(1)} + (K+1) \cdot J_{j,K,i,K+1}^{(2)}]}{r_n^2} \right\} \cdot \phi_i^{L,K+1} \end{aligned} \quad (2.189)$$

Using the result obtained in Equation (2.181) for $g_{jK,iK}^{(2)}(r_n)$

and that of Equation (2.142) for $g_{jK,iK}^{(3,1)}(r_n)$, one has

$$\begin{aligned}
\frac{d^2 \phi_j^{L,K}}{dr_n^2} - \left\{ \frac{V_{jK} - E}{\epsilon} + \frac{L(L+1) - K^2}{r_n^2} \right\} \phi_j^{LK} &= 2\pi \delta_{K,K'} \cdot \sum_i \left\{ \left[g_{jK,iK}^{(1,1)} \right. \right. \\
&+ K^2 g_{jK,iK}^{(1,2)} - \left. \frac{d Q_{jK,iK}^{(1)}}{dr_n} \right] \phi_i^{L,K} - 2 Q_{jK,iK}^{(1)} \frac{d \phi_i^{L,K}}{dr_n} \Bigg\} \\
&+ 2\pi \cdot \sum_{K'=0}^L \delta_{K',K\pm 1} \cdot \left[\frac{\delta_{K\pm 1,0} + \sqrt{2}(1-\delta_{K\pm 1,0})}{\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})} \right] \cdot [\sqrt{2}(\delta_{K,0} + \delta_{K\pm 1,0}) \\
&+ (1-\delta_{K,0})(1-\delta_{K\pm 1,0})] \cdot \sqrt{(L-K+\frac{1}{2}+\frac{1}{2})(L+K+\frac{1}{2}+\frac{1}{2})} \\
&\cdot \sum_i \left\{ \frac{\mathcal{J}_{j,K;i,K\pm 1}^{(1) \pm (K\pm 1)} \mathcal{J}_{j,K;i,K\pm 1}^{(2)}}{r_n^2} \right\} \cdot \phi_i^{L,K\pm 1} \quad (2.190)
\end{aligned}$$

One recalls from Equation (2.152) that $Q_{jK,jK}^{(1)}(r_n) = 0$, due to its antisymmetry in the indices jK and iK' ; consequently, the terms $g_{jK,jK}^{(1,1)}(r_n)$ and $g_{jK,jK}^{(1,2)}$ are the only terms which contribute to the diagonal or self-coupling parameter multiplying $\phi_j^{L,K}(r_n)$ in the differential equation for $\phi_j^{L,K}(r_n)$.

The terms $g_{jK,iK}^{(1,1)}(r_n)$ and $g_{jK,iK}^{(1,2)}(r_n)$ are symmetric in the indices j and i . The combination of terms $\{\mathcal{J}_{jK;i,K\pm 1}^{(1)}(r_n) \pm (K\pm 1) \cdot \mathcal{J}_{jK;i,K\pm 1}^{(2)}(r_n)\}$ is seen to be proportional to $\mathcal{J}_{j,K;i,K\pm 1}^{(1)}(r_n)$, which was shown in Equation (2.162) to be antisymmetrical in the indices jK and iK' for

$K'=K\pm 1$. The above observations concerning these symmetries and antisymmetries in the indices jK and iK' permit a great reduction in the time required to calculate a set of coupling parameters, because only the diagonal parameters and those for, say, $j < i$ and $K < K'$ need be computed. The remainder of the coupling parameters, those for which $j > i$ and $K > K'$, may then be obtained from the symmetry or antisymmetry of the terms involved.

In the following, one displays the explicit equations that are obtained for total orbital angular momentum $L=0$ and $L=1$.

For $L=0$, one needs only $K=0$ and $K'=0$, and the coupled equations reduce to

$$\begin{aligned} \frac{d^2 \phi_j^{0,0}}{dr_n^2} - \left\{ \frac{V_{j0}-E}{\epsilon} \right\} \phi_j^{0,0} = 2\pi \sum_i \left\{ \left[g_{j0,i0}^{(1,1)} - \frac{dQ_{j0,i0}^{(1)}}{dr_n} \right] \right. \\ \left. \cdot \phi_i^{0,0} - 2 \cdot Q_{j0,i0}^{(1)} \cdot \frac{d\phi_i^{0,0}}{dr_n} \right\} . \end{aligned} \quad (2.191)$$

For $L=1$, one needs $K=0,1$ and $K'=0,1$, which leads to the equations given below (recall that $K=0$ denotes a σ electronic state and $K=1$ denotes a Π electronic state):

for $L=1$ and $K=0$,

$$\begin{aligned} \frac{d^2 \phi_j^{1,0}}{dr_n^2} - \left\{ \frac{V_{j0}-E}{\epsilon} + \frac{2}{r_n^2} \right\} \phi_j^{1,0} = 2\pi \cdot \sum_i \left\{ \left[g_{j0,i0}^{(1,1)} - \frac{dQ_{j0,i0}^{(1)}}{dr_n} \right] \cdot \phi_i^{1,0} \right. \\ \left. - 2 \cdot Q_{j0,i0}^{(1)} \cdot \frac{d\phi_i^{1,0}}{dr_n} \right\} - (2\pi) \\ \cdot (2\sqrt{2}) \cdot \sum_i \left\{ \frac{\mathcal{J}_{j,0;i,1}^{(1)} + \mathcal{J}_{j,0;i,1}^{(2)}}{r_n^2} \right\} \phi_i^{1,1} , \end{aligned} \quad (2.192)$$

and for $L=1$ and $K=1$,

$$\begin{aligned} \frac{d^2 \phi_j^{1,1}}{dr_n^2} - \left\{ \frac{V_{j1} - E}{\epsilon} + \frac{1}{r_n^2} \right\} \phi_j^{1,1} = 2\pi \cdot \sum_i \left\{ \left[g_{j1,i1}^{(1,1)} \right. \right. \\ \left. \left. + g_{j1,i1}^{(1,2)} - \frac{dQ_{j1,i1}^{(1)}}{dr_n} \right] \phi_i^{1,1} - 2Q_{j1,i1}^{(1)} \frac{d\phi_i^{1,1}}{dr_n} \right\} \\ + (2\pi) \cdot (\sqrt{2}) \cdot \sum_i \frac{J_{j,1;i,0}^{(1)}}{r_n^2} \phi_i^{1,0} \end{aligned} \quad (2.193)$$

Note that $J_{j,1;i,0}^{(1)} = -\{J_{i,0;j,1}^{(1)} + J_{i,0;j,1}^{(2)}\}$ from Equation (2.154).

Equation (2.191) or Equations (2.192) and (2.193) may be condensed by defining, in the case of Equation (2.191), the coupling coefficients

$$a_{ji}(r_n) = 2\pi \left\{ g_{ji}(r_n)^{(1,1)} - \frac{d}{dr_n} R_{ji}(r_n)^{(1)} \right\}, \quad (2.194)$$

and

$$b_{ji}(r_n) = 2\pi \left\{ -2R_{ji}(r_n)^{(1)} \right\}. \quad (2.195)$$

Then the coupled equations take the form

$$\begin{aligned} \frac{d^2 \phi_j(r_n)}{dr_n^2} - \frac{1}{\epsilon} \{V_j(r_n) - E\} \phi_j(r_n) = \sum_i \left\{ a_{ji}(r_n) \cdot \phi_i(r_n) \right. \\ \left. + b_{ji}(r_n) \cdot \frac{d\phi_j(r_n)}{dr_n} \right\}. \end{aligned} \quad (2.196)$$

In a matrix form the equations are

$$(\overline{O} + \frac{E}{\epsilon})\vec{\phi} = \left(\overline{A} + \overline{B} \frac{d}{dr_n} \right) \vec{\phi}, \quad (2.197)$$

where

$$\overline{O} = \begin{pmatrix} \frac{d^2}{dr_n^2} - \frac{1}{\epsilon} V_1(r_n) & | & 0 & | & 0 & | & \dots \\ 0 & | & \frac{d^2}{dr_n^2} - \frac{1}{\epsilon} V_2(r_n) & | & 0 & | & \dots \\ 0 & | & 0 & | & \frac{d^2}{dr_n^2} - \frac{1}{\epsilon} V_3(r_n) & | & 0 & \dots \end{pmatrix},$$

$$\overline{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \dots \\ a_{21} & a_{22} & a_{23} \dots \\ a_{31} & a_{32} & a_{33} \dots \\ \vdots & \vdots & \vdots \end{pmatrix},$$

$$\overline{B} = \begin{pmatrix} 0 & b_{12} & b_{13} \dots \\ -b_{12} & 0 & b_{23} \dots \\ -b_{13} & -b_{23} & 0 \dots \\ \vdots & \vdots & \vdots \end{pmatrix},$$

and

$$\vec{\phi} = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \vdots \end{pmatrix}.$$

CHAPTER III

NUMERICAL TECHNIQUES AND FORMULAS

The following work emphasizes the numerical procedures that were used to compute the wave functions and those physical quantities derived from the wave functions. Formulas are obtained for the overlap γ and the quadrupole moment Q .

I. NUMERICAL SOLUTION FOR THE ELECTRONIC STATES

The numerical evaluation of the electronic expansion coefficients and parameters (Bates, Ledsham, and Stewart, 1953) derived in Chapter II is developed below. Consider first the "inner" function $M_i(n, r_n)$. The coefficients $f_n^{(i)}(r_n)$ are obtained from the three-term recursion formula

$$a_n f_{n+2}^{(i)} - b_n f_n^{(i)} + c_n f_{n-2}^{(i)} = 0, \quad (3.1)$$

where

$$a_n = \frac{(n+2m+2)(n+2m+1)}{(2n+2m+5)(2n+2m+3)} \cdot [p_i(r_n)]^2, \quad (3.2)$$

$$b_n = A_i(r_n) + (m+n) \cdot (m+n-1) - \frac{(2n) \cdot (n+2m+1) + 2m-1}{(2n+2m-1)(2n+2m+3)} \cdot [p_i(r_n)]^2, \quad (3.3)$$

and

$$c_n = \frac{(n-1)(n)}{(2n+2m-3)(2n+2m-1)} \cdot [p_i(r_n)]^2. \quad (3.4)$$

In the above, $A_i(r_n)$ is a parameter arising from the separation of variables for the assumed form of the solution. Along with the parameter $\sigma_i(r_n)$, these parameters determine the three-term recursion formula for the $y_i(\zeta, r_n)$ function in the "outer" function $\Lambda_i(\xi, r_n)$:

$$\alpha_t g_{t+1}^{(i)} - \beta_t g_t^{(i)} + \gamma_t g_{t-1}^{(i)} = 0, \quad (3.5)$$

in which

$$\alpha_t = (t+1) \cdot (t+m+1), \quad (3.6)$$

$$\begin{aligned} \beta_t = & 2t^2 + [4p_i(r_n) - 2\sigma_i(r_n)]t - 2p_i(r_n) \cdot \sigma_i(r_n) \\ & - [m+1] \cdot (m+\sigma_i(r_n)) - A_i(r_n) + [p_i(r_n)]^2, \end{aligned} \quad (3.7)$$

and

$$\gamma_t = [t-m-\sigma_i(r_n)-1] \cdot [t-\sigma_i(r_n)-1]. \quad (3.8)$$

The three-term recursion formula for the $M_i(n, r_n)$ expansion coefficients may be expressed as

$$a_n \frac{f_{n+2}}{f_n} - b_n + \frac{c_n}{\frac{f_n}{f_{n-2}}} = 0, \quad (3.9)$$

in which the superscripts have been dropped.

Let

$$F_n = \frac{f_n}{f_{n-2}} \quad (3.10)$$

Then,

$$F_n = \frac{c_n}{b_n - a_n \cdot F_{n+2}} ; \quad (3.11)$$

i.e., the recursion formula has been expressed as a continued fraction.

Defining the inverse continued fraction as

$$G_n = \frac{1}{F_n} = \frac{f_{n-2}}{f_n} , \quad (3.12)$$

one has

$$G_{n+2} = \frac{a_n}{b_n - c_n G_n} \quad (3.13)$$

An approximation to the value of the continued fraction F_{n+2} may be found for large values of n , from which one may obtain a value of F_n . This process may be iterated from a large value of n to a small value, say n^*+2 . In a similar manner, the value of G_2 may be calculated directly, from which one obtains the values $G_4, G_6, \dots G_{n^*}$ by iteration. In particular

$$G_2 = \frac{f_0}{f_2} = \frac{a_0}{b_0} , \quad (3.14)$$

and

$$a_{n*} F_{n*+2} - b_{n*} + c_{n*} G_{n*} = 0 \quad (3.15)$$

becomes the requirement for self-consistency.

Recall that the coefficients a_n , b_n , and c_n are functions of the parameters p_i and A_i , where the argument has been dropped. At a given value of the parameter p_i there exists an eigenvalue of A_i for which the expression above is self-consistent. Thus one assumed a value of p_i and a value of A_i , calculated the corresponding values of F_{n*+2} and G_{n*} , tested the validity of the above self-consistency requirement, and corrected the value of A_i . This process was iterated in the present work until the correction to A_i at a given p_i was less than one part in 10^7 , $\left| \frac{\delta A_i}{A_i} \right| < 10^{-7}$.

The recursion formula for the expansion coefficients of $y_i(\zeta, r_n)$ in $\Lambda_i(\xi, r_n)$ may be posed in a similar manner (dropping superscripts and arguments):

$$F_t = \frac{g_t}{g_{t-1}} = \frac{\gamma_t}{\beta_t - \alpha_t F_{t+1}} \quad (3.16)$$

and

$$G_t = \frac{1}{F_t} = \frac{g_{t-1}}{g_t} \quad (3.17)$$

yields

$$G_{t+1} = \frac{\alpha_t}{\beta_t - \gamma_t G_t} \quad (3.18)$$

At some value of the index, say $t = t^*$, the self-consistency equation is

$$\alpha_{t^*} F_{t^*+1} - \beta_{t^*} + \gamma_{t^*} G_{t^*} = 0 \quad (3.19)$$

Using the values of p_i and A_i that had already been determined for the $M_i(n, r_n)$ function, one assumed a value of σ_i , calculated F_{t^*+1} and G_{t^*} , tested self-consistency, and corrected the value of σ_i . This process, too, was iterated in the present work until the correction to σ_i at given values of p_i and A_i was less than one part in 10^7 ($|\frac{\delta\sigma}{\sigma}| < 10^{-7}$).

Noting from Equation (2.39) that

$$r_n = p_i(r_n) \cdot [\sigma_i(r_n) + m + 1] \quad (3.20)$$

the value of r_n corresponding to the values of p_i and σ_i may be calculated. The values of p_i , A_i , and σ_i were then adjusted by the above iterative processes until the value of r_n differed from that of a preselected mesh point by less than one part in 10^7 . The values of r_n were increased in steps of $0.05 a_\mu$ from $0a_\mu$ to $20a_\mu$ in the present work; the resultant values of $p_i(r_n)$, $A_i(r_n)$, and $\sigma_i(r_n)$ were used to calculate the electronic energy

$W_i(r_n)$ from the relation (Equations 2.35 and 3.20)

$$W_i(r_n) = -\left(\frac{2}{\sigma_i(r_n) + m + 1}\right)^2 \quad (3.21)$$

Corresponding to these values of p_i , A_i , and σ_i and the values of the continued fractions, the first ten non-zero coefficients $f_n^{(i)}(r_n)$ in the expansion for $M_i(n, r_n)$ were calculated. It was found that the inverse continued fraction G_n was numerically stable from $n=2$ (or 3) to G_{n^*} , where f_{n^*} is the coefficient which is largest in absolute value. Conversely, the continued fraction F_n was found to be stable from large n (here taken to be about 80) to F_{n^*+2} , n^* again labeling the coefficient largest in absolute value. Thus, the coefficient f_{n^*} was initially defined to be unity, and the other coefficients were calculated from

$$f_{n-2} = G_n \cdot f_n, \quad n - 2 < n^*, \quad (3.22)$$

and

$$f_{n+2} = F_{n+2} \cdot f_n, \quad n + 2 > n^*. \quad (3.23)$$

The quantity $\int_{n=-1}^1 |M_i'(n, r_n)|^2 dn$, where the prime implies that the

functions are not normalized, was then calculated by numerical Legendre-Gaussian integration (Hildebrand, 1956). Each coefficient f_n' was multiplied by the inverse of the square root of this integral, such that coefficients for the function $M_i(\eta, r_n)$, having the proper normalization, were obtained.

Similarly, the first ten coefficients $g_t^{(i)}(r_n)$ in the expansion of $y_i(\zeta, r_n)$ for $\Lambda_i(\xi, r_n)$ were calculated by assuming the coefficient g_{t*} , which is largest in absolute value, to be unity. Again, the continued fraction G_t was found to be numerically stable as t increased from 1 to $t \leq t^*$, and F_t was stable as t decreased from about 300 to $t \geq t^* + 1$. The other coefficients are then calculated from

$$g_{t-1} = G_t g_t, \quad t - 1 < t^*; \quad (3.24)$$

$$g_{t+1} = F_{t+1} g_t, \quad t + 1 > t^*. \quad (3.25)$$

The quantity $\int_{\xi=1}^{\infty} |\Lambda_i'(\xi, r_n)|^2 d\xi$, where the prime implies that the functions are not normalized, was calculated by numerical Laguerre-Gaussian integration (Hildebrand, 1956). Each coefficient g_t' was multiplied by the inverse of the square root of this integral, such that the final function $\Lambda_i(\xi, r_n)$ has the proper normalization.

Finally, an integration over the volume element in the electronic coordinate space was performed to obtain the normalization constant $\mathcal{N}_i(r_n)$:

$$\frac{1}{[\mathcal{N}_i(r_n)]^2} = \int_{R_\mu} d^3R_\mu |\Lambda_i(\xi, r_n) \cdot M_i(\eta, r_n) \cdot \Phi_i(\phi)|^2 \quad (3.26)$$

The integration over ϕ was done analytically. It is worth noting that the above integration separates so that one has only to perform one-dimensional numerical integrations. This property of separation of the volume integrals in the electronic coordinate space was found for all the quantities calculated in the work for the homonuclear case.

II. NUMERICAL SOLUTION OF THE ROTATIONAL AND VIBRATIONAL STATES FOR THE EQUAL-MASS (HOMONUCLEAR) CASE

The relationship of the programs used to effect a solution of the three-body problem is shown in Figure 2 page 91. The values of the electronic parameters were calculated on the interval from $r_n = 0.05a_\mu$ to $20a_\mu$ in increments of $0.05a_\mu$, as described above. One tape was made by the programs WØFR and NØRMJI for each electronic state, containing the electronic parameters, expansion coefficients, normalization constants, and their derivatives with respect to r_n .

The coupling parameters developed above were calculated in the program KPARAM by numerical integration over the electronic variables ξ and η at the same 400 mesh points, $r_n = 0.05 (0.05) 20.00a_\mu$. At each mesh point

FIGURE 2

PROGRAMS USED TO EFFECT SOLUTION FOR
HYDROGEN MOLECULAR ION

a maximum of 24 integrals, needed for evaluation of the coupling parameters, were calculated for the $M_i(\eta, r_n)$ functions by Legendre-Gaussian integration (Hildebrand, 1956). The corresponding integrals then were calculated at each mesh point for the $\Lambda_i(\xi, r_n)$ functions by Laguerre-Gaussian integration (Hildebrand, 1956). The integrals were then combined to form the coupling parameters. Six tapes made by NØRMJI, one for each electronic state, were used by KPARAM to calculate the diagonal and upper-diagonal coupling parameters. The lower-diagonal parameters were obtained by symmetry. The execution time required to generate the coupling parameters for six electronic states was about thirteen hours on the IBM 7090 computer.

These coupling parameters were combined by the program SETUP to form the coefficient $a_{ji}(r_n)$, which multiplies a coupled vibrational element $\phi_i^{LK}(r_n)$ in the coupled differential equations, and the coefficient $b_{ji}(r_n)$, which multiplies $\frac{d\phi_i^{LK}}{dr_n}$. This program also merged the coupling coefficients such that, at a given value of r_n (a "mesh point"), all the required coupling coefficients were available on a tape.

The tape made by SETUP was then fed to the program SØLVDE to calculate solutions to the coupled ordinary differential equations. The following is a description of the numerical methods used in the solution of these equations.

III. RADIAL WAVE FUNCTIONS FOR THE BOUND STATE SOLUTIONS

Let N be the number of elements $\phi_j^L(r_n)$, $1 \leq j \leq N$, which are to be coupled together, as in Equation (2.196). In principle, the number N is infinite; however, one must truncate the series in order to perform a calculation. Let the case of one radial differential equation ($N = 1$), not including the diagonal coupling term $a_{jj}(r_n) \phi_j^L(r_n)$, be called the Born-Oppenheimer approximation. (The Born-Oppenheimer approximation will be defined as $N = 0$ on pp. 147 ff. to distinguish it from the adiabatic approximation.) Let the adiabatic approximation be defined as one differential equation ($N = 1$), including the diagonal coupling term $a_{jj}(r_n) \phi_j^L(r_n)$ and no others. Recall that $b_{jj}(r_n)$ is identically equal to zero, so that the coupling to $\frac{d\phi_j^L(r_n)}{dr_n}$ need not be considered for either of the above cases. Finally, let the case of $N \geq 2$ coupled differential equations be called the coupled equations of order N . In the following, one drops the argument r_n from the functions, coupling coefficients, and potentials.

The form of the N coupled differential equations indicates that, in general, there exist $2N$ vectors $\vec{\phi}^L$ which are complementary solutions to the equations at a given value of the energy E . Application of the bound state boundary conditions $\vec{\phi}^L(r_n = 0) = 0$ and $\vec{\phi}^L(r_n \rightarrow \infty) = 0$ makes the system of equations an eigenvalue problem for the energy E and limits the number of complementary solutions required to N vectors $\vec{\phi}^L$ which are regular at the origin, $r_n = 0$, and at infinity, $r_n \rightarrow \infty$.

The numerical solution of a differential equation is stable to numerical integration away from a singular point. The terms involving $\frac{1}{r_n^2}$ and $\frac{1}{r_n}$ in the centrifugal barrier and the internuclear repulsion, respectively, make $r_n = 0$ a (regular) singular point in the radial equations. The form of the radial equations, transformed to $\frac{1}{r_n}$, demonstrates that $\frac{1}{r_n} = 0$ is a singular point corresponding to $r_n \rightarrow \infty$.

In order to effect a numerical solution to the radial equation, coupled or uncoupled, one may integrate numerically from a small value $r_n = r_{n_1} \approx 0$ to a larger value $r_n = r_m$, which lies within the classically allowed region of the effective potential, preferably near an extremum of the wave function. Let $r_n = r_m$ be called the match point. Another solution may be obtained by numerical integration from a large value $r_n = r_{n_2} \gg r_m$ to $r_n = r_m$, the match point. At the match point these complementary solutions for both regions may then be joined to form a single solution vector $\vec{\phi}^L$ continuous in, say, the values of $\vec{\phi}^L$ and all but one of the elements of $\frac{d\vec{\phi}^L}{dr_n}$. Only at an eigenvalue of the energy E will all elements of $\frac{d\vec{\phi}^L}{dr_n}$ be continuous at the match point. Further, the discontinuity may be related by a generalization of the Hartree corrector to the desired quantitative correction to E to make E lie nearer an eigenvalue. The process may be iterated until the energy correction is as small as is warranted by the accuracy of the potential (Cohen, Judd, and Riddell, 1960a).

An alternative method of solution is presented in the work of Fox (1960) and Cohen, Coulson, and Fox (1961). However, it was chosen to use the method outlined above.

The numerical integration scheme used in this study for the coupled ordinary differential equations is Gill's formulation (Gill, 1951) of the Runge-Kutta process. The Runge-Kutta-Gill process offers the advantages of stability and accuracy. This process is based on a Taylor series expansion of $\phi(r_n)$ about the mesh point $r_n = r_0$, which yields the value of the function $\phi(r_n = r_0 + \Delta r)$ at the next mesh point, keeping terms of order $O(\Delta r^4)$. It is a point-slope process requiring, for second-order differential equations, a knowledge of the value of $\phi(r_0)$ and $\frac{d\phi(r_0)}{dr_n}$. In addition, the values of the potentials and coupling parameters must be known at the ends and mid-point of each interval. The step size Δr was chosen to be $0.10a_\mu$ for the (pup)⁺ case to correspond to coupling coefficient tape which was made in increments of $0.05a_\mu$. Other step sizes were created by interpolation of the coupling coefficients and the electronic energies.

IV. INITIALIZATION OF RADIAL WAVE FUNCTIONS

As a consequence of having chosen the Runge-Kutta-Gill process the values at the initial point $r_n = r_{n_1}$ of all the elements $\phi_j^L(r_{n_1})$ and $\frac{d\phi_j^L(r_{n_1})}{dr_n}$, $j=1,N$, must be specified. The process cannot be started at $r_{n_1}=0$ with $\phi_j^L(0)=0$ and $\frac{d\phi_j^L(0)}{dr_n}=0$, because only the trivial results

$\phi_j^L(r_n)=0$ and $\frac{d\phi_j^L(r_n)}{dr_n} = 0$ are obtained. Thus, one uses a Frobenius series solution or a perturbation approximation evaluated at r_{n_1} to start the outward integration. The perturbation approximation is useful, if r_1 must be chosen fairly large, because many terms would be required in the Frobenius series solution about the origin to achieve a comparable result.

Using either method, one must obtain N vectors $\vec{\phi}_i^L(r_1)$ for the coupled solution of order N , $i=1,N$, which are linearly independent and are regular at the origin. The method outlined below follows more naturally from the perturbation viewpoint.

There are N elements in the i -th vector $\vec{\phi}_i^L$; let the j -th element of the i -th vector be labeled by the index j : $\phi_{j,i}^{LK}$. Assume that $\phi_{j,j}^{LK}$ is considerably larger than the other elements $\phi_{t \neq j,j}^{LK}$ in the j -th vector, corresponding to dominance of the solution of the j -th vector by the j -th differential equation of the coupled system of equations. If the j -th element is the largest, the values of the other elements of the j -th vector are determined chiefly by their interaction with the j -th element. As an approximation, one may neglect the interaction of the elements $\phi_{t \neq j,j}^{LK}$ with each other and consider the pair of differential equations

$$\frac{d^2 \phi_{j,j}^{LK}}{dr_n^2} + G_j(r_n) \phi_{j,j}^{LK} = a_{jt}(r_n) \phi_{t,j}^{LK} + b_{jt}(r_n) \frac{d\phi_{t,j}^{LK}}{dr_n}, \quad (3.26)$$

$$\frac{d^2 \phi_{t,j}^{LK_t}}{dr_n^2} + G_t(r_n) \phi_{t,j}^{LK_t} = a_{tj}(r_n) \phi_{j,j}^{LK_j} + b_{tj}(r_n) \frac{d\phi_{j,j}^{LK_j}}{dr_n}, \quad t \neq j, \quad (3.27)$$

where

$$G_j(r_n) = \frac{E - V_j(r_n)}{\epsilon} - \left\{ \frac{L(L+1) - K_j^2}{r_n^2} + a_{jj}(r_n) \right\} \quad (3.28)$$

and

$$G_t(r_n) = \frac{E - V_t(r_n)}{\epsilon} - \left\{ \frac{L(L+1) - K_t^2}{r_n^2} + a_{tt}(r_n) \right\}. \quad (3.29)$$

Recall that r_{n_1} was assumed to have been chosen fairly large, of the order of $0.3a_\mu$. The local variation of the effective potentials $G_j(r_n)$ and $G_t(r_n)$ and of the coupling coefficients a_{ji} and b_{ji} is small over the interval of one step size Δr . For the interval $r_{n_1} - \frac{\Delta r}{2} < r_n < r_{n_1} + \frac{\Delta r}{2}$, the values of the effective potentials and the coupling coefficients, evaluated at $r_n = r_{n_1}$, thus represent the lowest order term of a Taylor series expansion about r_{n_1} . Let $\phi_{t,j}^{LK_t} = \epsilon h_{t,j}^{(1)} \phi_{j,j}^{LK_j}$; one has from Equation (3.26)

$$\frac{d^2 \phi_{j,j}^{LK_j}}{dr_n^2} + G_j(r_{n_1}) \phi_{j,j}^{LK_j} = \epsilon h_{t,j}^{(1)} \left[a_{jt}(r_{n_1}) \phi_{j,j}^{LK_j} + b_{jt}(r_{n_1}) \frac{d\phi_{j,j}^{LK_j}}{dr_n} \right]. \quad (3.30)$$

Keeping those terms not multiplied by the smallness parameter ϵ , one obtains

$$\phi_{j,j}^{LK_j}(r_{n_1}) = a_j^{(1)} e^{k_j^{(1)} r_{n_1}}, \quad (3.31)$$

where $q_j^{(1)}$ is an integration constant, the plus sign in the exponential has been chosen because the wave function is required by the boundary condition to be growing in integration toward the classically allowed region, and

$$k_j^{(1)} = \sqrt{G_j(r_{n_1})} . \quad (3.32)$$

From Equation (3.27) one obtains

$$\begin{aligned} & \epsilon k_j^2 h_{t,j}^{(1)} \phi_{j,j}^{LK_j} + [E - V_t(r_{n_1})] h_{t,j}^{(1)} \phi_{j,j}^{LK_j} - \epsilon \left\{ \frac{L(L+1) - K_t^2}{r_{n_1}^2} \right. \\ & \left. + a_{tt}(r_{n_1}) \right\} h_{t,j}^{(1)} \phi_{j,j}^{LK_j} \\ & = a_{tj}(r_{n_1}) \phi_{j,j}^{LK_j} + k_j^{(1)} b_{tj}(r_{n_1}) \phi_{j,j}^{LK_j}, \quad t \neq j . \end{aligned} \quad (3.33)$$

Again keeping only those terms not multiplied by ϵ , one obtains

$$h_{t,j}^{(1)} = \frac{a_{tj}(r_{n_1}) + k_j^{(1)} b_{tj}(r_{n_1})}{E - V_t(r_{n_1})}, \quad t \neq j. \quad (3.34)$$

To summarize, one has found for the outward integration

$$\phi_{j,j}^{LK_j}(r_{n_1}) = q_j e^{k_j^{(1)} r_{n_1}}, \quad (3.31)$$

and

$$\phi_{t,j}^{LK_t}(r_{n_1}) = \epsilon h_{t,j}^{(1)} \phi_{j,j}^{LK_j}(r_{n_1}), \quad t \neq j, \quad (3.35)$$

from which one obtains

$$\frac{d\phi_{j,j}^{LK}(r_{n_1})}{dr_n} = k_j^{(1)} \phi_{j,j}^{LK}(r_{n_1}) \quad (3.36)$$

and

$$\frac{d\phi_{t,j}^{LK}(r_{n_1})}{dr_n} = k_j^{(1)} \phi_{t,j}^{LK}(r_{n_1}), \quad t \neq j. \quad (3.37)$$

For $N=3$, the above procedure results in a set of three vectors initialized at $r_n=r_{n_1}$ with the values

$$\vec{\phi}_1(r_{n_1}) = \begin{pmatrix} 1 \\ \epsilon h_{21}^{(1)} \\ \epsilon h_{31}^{(1)} \end{pmatrix} \phi_{11}^{LK_1}(r_{n_1}), \quad \frac{d\vec{\phi}_1^L(r_{n_1})}{dr_n} = k_1^{(1)} \vec{\phi}_1^L(r_{n_1}); \quad (3.38)$$

$$\vec{\phi}_2^L(r_{n_1}) = \begin{pmatrix} \epsilon h_{12}^{(1)} \\ 1 \\ \epsilon h_{32}^{(1)} \end{pmatrix} \phi_{22}^{LK_2}(r_{n_1}), \quad \frac{d\vec{\phi}_2^L(r_{n_1})}{dr_n} = k_2^{(1)} \vec{\phi}_2^L(r_{n_1}); \quad (3.39)$$

and

$$\vec{\phi}_3^L(r_{n_1}) = \begin{pmatrix} \epsilon h_{13}^{(1)} \\ \epsilon h_{23}^{(1)} \\ 1 \end{pmatrix} \phi_{33}^{LK_3}, \quad \frac{d\vec{\phi}_3^L(r_{n_1})}{dr_n} = k_3^{(1)} \vec{\phi}_3^L(r_{n_1}). \quad (3.40)$$

The vectors $\vec{\phi}_1^L, \vec{\phi}_2^L, \dots, \vec{\phi}_N^L$ are not coupled with each other after initialization. Each vector represents one of the complementary functions required to obtain the general solution of the system of equations.

The initialization of a different set of N complementary vectors

$\vec{\phi}_i^L(r_{n_2}); i=N+1, N+2, \dots, 2N$; at large $r_n=r_{n_2}$ for the inward integration

may be accomplished by a procedure similar to that given above. The sign in

the exponential has to be taken negative to satisfy the boundary condition

$\vec{\phi}^L(r_n \rightarrow \infty) \rightarrow 0$. One obtains

$$\phi_{j,j}^{L,K_j}(r_{n_2}) = q_j^{(2)} e^{-k_j^{(2)} r_{n_2}} ; \quad (3.41)$$

$$\phi_{t,j}^{L,K_t}(r_{n_2}) = \epsilon h_{t,j}^{(2)} \phi_{j,j}^{L,K_j}(r_{n_2}), \quad t \neq j ; \quad (3.42)$$

$$\frac{d\phi_{j,j}^{L,K_j}(r_{n_2})}{dr_n} = -k_j^{(2)} \phi_{j,j}^{L,K_j}(r_{n_2}) ; \quad (3.43)$$

and

$$\frac{d\phi_{t,j}^{LK_j}(r_{n_2})}{dr_n} = -k_j^{(2)} \phi_{t,j}^{LK_t}(r_{n_2}), \quad t \neq j ; \quad (3.44)$$

where $q_j^{(2)}$ is a constant of integration,

$$k_j^{(2)} = \sqrt{G_j(r_{n_2})} , \quad (3.45)$$

and

$$h_{t,j}^{(2)} = \frac{a_{tj}(r_{n_2}) - k_j^{(2)} b_{t,j}(r_{n_2})}{E - V_t(r_{n_2})} . \quad (3.46)$$

For $N=3$, the above procedure results in the set of three vectors

$\vec{\phi}_4^L(r_{n_2})$, $\vec{\phi}_5^L(r_{n_2})$, and $\vec{\phi}_6^L(r_{n_2})$ along with their derivatives:

$$\vec{\phi}_4^L(r_{n_2}) = \begin{pmatrix} 1 \\ \epsilon h_{21}^{(2)} \\ \epsilon h_{31}^{(2)} \end{pmatrix} \phi_{11}^{LK_1}(r_{n_2}) , \quad \frac{d\vec{\phi}_4^L(r_{n_2})}{dr_n} = -k_1^{(2)} \vec{\phi}_4^L(r_{n_2}) ; \quad (3.47)$$

$$\vec{\phi}_5^L(r_{n_2}) = \begin{pmatrix} \epsilon h_{12}^{(2)} \\ 1 \\ \epsilon h_{32}^{(2)} \end{pmatrix} \phi_{22}^{LK_2}(r_{n_2}), \quad \frac{d\vec{\phi}_5^L(r_{n_2})}{dr_n} = -k_2^{(2)} \vec{\phi}_5^L(r_{n_2}) \quad ; \quad (3.48)$$

and

$$\vec{\phi}_6^L(r_{n_2}) = \begin{pmatrix} \epsilon h_{13}^{(2)} \\ \epsilon h_{23}^{(2)} \\ 1 \end{pmatrix} \phi_{33}^{LK_3}(r_{n_2}), \quad \frac{d\vec{\phi}_6^L(r_{n_2})}{dr_n} = -k_3^{(2)} \vec{\phi}_6^L(r_{n_2}) \quad . \quad (3.49)$$

V. JOINING PROCEDURE AND ENERGY CORRECTION

Numerical integration of the coupled equations outward from r_{n_1} to the match point r_m yields the N complementary vectors $\vec{\phi}_1^L(r_m), \vec{\phi}_2^L(r_m), \dots, \vec{\phi}_N^L(r_m)$ and their derivatives with respect to r_n . Similarly, inward integration from r_{n_2} to the match point r_m yields N more complementary vectors $\vec{\phi}_{N+1}^L(r_m), \vec{\phi}_{N+2}^L(r_m), \dots, \vec{\phi}_{2N}^L(r_m)$ and their derivatives. One seeks a solution $\vec{\phi}^L(r_n)$ in the region $r_{n_1} \leq r_n \leq r_m$:

$$\vec{\phi}^L(r_n) = \sum_{i=1}^N \vec{\phi}_i^L(r_n) C_i \quad (3.50)$$

and

$$\frac{d\vec{\phi}^L(r_n)}{dr_n} = \sum_{i=1}^N \frac{d\vec{\phi}_i^L(r_n)}{dr_n} C_i \quad (3.51)$$

Similarly, in the region $r_m \leq r_n \leq r_{n_2}$ one seeks

$$\vec{\phi}^L(r_n) = \sum_{i=N+1}^{2N} \vec{\phi}_i^L(r_n) C_i \quad (3.52)$$

and

$$\frac{d\vec{\phi}^L(r_n)}{dr_n} = \sum_{i=N+1}^{2N} \frac{d\vec{\phi}_i^L(r_n)}{dr_n} C_i \quad (3.53)$$

In particular, the composite function $\vec{\phi}^L(r_n)$ and its derivative with respect to r_n are required to be continuous at the match point r_m :

$$\lim_{\delta r_n \rightarrow 0} \frac{d\vec{\phi}^L(r_m - \delta r_n)}{dr_n} = \lim_{\delta r_n \rightarrow 0} \frac{d\vec{\phi}^L(r_m + \delta r_n)}{dr_n} \quad (3.54)$$

and

$$\lim_{\delta r_n \rightarrow 0} \vec{\phi}^L(r_m - \delta r_n) = \lim_{\delta r_n \rightarrow 0} \vec{\phi}^L(r_m + \delta r_n). \quad (3.55)$$

Substitution of Equations (3.51) and (3.53) in Equation (3.54) yields

$$\sum_{i=1}^N \frac{d\vec{\phi}_i^L(r_m)}{dr_n} C_i = \sum_{i=N+1}^{2N} \frac{d\vec{\phi}_i^L(r_m)}{dr_n} C_i. \quad (3.56)$$

Substitution of Equations (3.50) and (3.52) in Equation (3.55) yields

$$\sum_{i=1}^N \vec{\phi}_i^L(r_m) C_i = \sum_{i=N+1}^{2N} \vec{\phi}_i^L(r_m) C_i. \quad (3.57)$$

These equations can be combined in the matrix equation

$$\bar{U} \vec{c} = 0; \quad (3.58)$$

where the upper half of the $2N \times 2N$ matrix $\bar{U}$ is composed of derivatives

$$U_{ji} = \frac{d\vec{\phi}_{j,i}^L(r_m)}{dr_n}; \quad j = 1, N; i = 1, 2N; \text{ and the lower half is composed of}$$

functions $U_{N+j,i} = \vec{\phi}_{j,i}^L(r_m); j = 1, N; i = 1, 2N$. Corresponding to the two regions, the vector $\vec{c}$ has the upper half of its elements directly equal those of $\vec{c}$: $c'_i = c_i, i = 1, N$; and the lower half of its elements equal the negative of those of $\vec{c}$: $c'_i = -c_i, i = N+1, 2N$. One has, letting

$$\frac{d\vec{\phi}_{ji}^L(r_m)}{dr_n} = \vec{\phi}'_{j,i} \quad \text{and} \quad \vec{\phi}_{j,i}^L(r_m) = \vec{\phi}_{j,i}, \quad (3.59)$$

$$\bar{U} = \begin{pmatrix} \phi'_{1,1} \cdots \phi'_{1,n} & \phi'_{1,N+1} \cdots \phi'_{1,2N} \\ \vdots & \vdots \\ \phi'_{N,1} \cdots \phi'_{N,N} & \phi'_{N,N+1} \cdots \phi'_{N,2N} \\ \phi_{1,1} \cdots \phi_{1,N} & \phi_{1,N+1} \cdots \phi_{1,2N} \\ \vdots & \vdots \\ \phi_{N,1} \cdots \phi_{N,N} & \phi_{N,N+1} \cdots \phi_{N,2N} \end{pmatrix} \quad (3.60)$$

and

$$\vec{c} = \begin{pmatrix} c_1 \\ \vdots \\ c_N \\ -c_{N+1} \\ \vdots \\ -c_{2N} \end{pmatrix}. \quad (3.61)$$

For a non-trivial vector $\vec{c}$, Equation (3.58) is true only if the determinant of $\bar{U}$ is zero:

$$|\bar{U}| = 0. \quad (3.62)$$

The vanishing of this determinant implies that each of the elements of $\vec{\phi}^L$ is continuous at the match point r_m , and it can vanish only if the total energy E of the system is an eigenvalue.

In general, the initial value of the energy E will not have been chosen to exactly equal an eigenvalue; consequently, the value of $|\bar{U}|$ will not equal zero. In this case, one may require the values of all but one of the elements:

of $\vec{\phi}^L(r_m)$ and $\frac{d\vec{\phi}^L(r_m)}{dr_n}$ to be continuous; from this function a correction to the energy is calculated below.

In order to put the discontinuity in the j_1 -th element of the vector $\frac{d\vec{\phi}^L(r_m)}{dr_n}$, $\frac{d\vec{\phi}^L}{dr_n}_{j_1}(r_m)$, let $c'_{j_1} \equiv 1$. Omitting the equation that requires continuity of the j_1 -th element of $\frac{d\vec{\phi}^L(r_m)}{dr_n}$, one has the system of $2N-1$ equations composed of

$$\sum_{i=1}^{2N} \phi'_{ji} c'_i = 0, \quad 1 \leq j \neq j_1 \leq N, \quad (3.63)$$

and the unchanged equations

$$\sum_{i=1}^{2N} \phi_{ji} c'_i = 0, \quad 1 \leq j \leq N. \quad (3.64)$$

Transposition to the right hand side of the elements multiplied by c'_{j_1} , which has been defined to be unity, yields

$$\sum_{\substack{i=1 \\ i \neq j_1}}^{2N} \phi'_{ji} c'_i = -\phi'_{j,j_1}, \quad 1 \leq j \neq j_1 \leq N, \quad (3.65)$$

and

$$\sum_{\substack{i=1 \\ i \neq j_1}}^{2N} \phi_{ji} c'_i = -\phi_{j,j_1}, \quad 1 \leq j \leq N. \quad (3.66)$$

This set of equations is equivalent to the matrix equation

$$\bar{A}_{j_1} \vec{x}_{j_1} = \vec{b}_{j_1}, \quad (3.67)$$

where the $(2N-1) \times (2N-1)$ matrix $\bar{A}_{j_1}$ is the minor of the j_1, j_1 element of $\bar{U}$ and the vector $\vec{x}_{j_1}$, composed of $2N-1$ elements, is the vector $\vec{c}$ with the j_1 -th element omitted. The vector $\vec{b}_{j_1}$ is the negative of the j_1 -th column of $\bar{U}$, omitting the element of the j_1 -th row. One can solve for $\vec{x}_{j_1}$ by pre-multiplying by the inverse of $\bar{A}_{j_1}$:

$$\vec{x}_{j_1} = \bar{A}_{j_1}^{-1} \vec{b}_{j_1}, \text{ if } |\bar{A}_{j_1}| \neq 0. \quad (3.68)$$

The vector $\vec{x}_{j_1}$ can be converted back to $\vec{c}$ by inserting a unit element between the elements j_1-1 and j_1 of $\vec{x}_{j_1}$ and changing the sign of the last N elements.

Since $\vec{c}$ can be found, one can calculate the unnormalized functions $\vec{\phi}^L(r_n)$ and $\frac{d\vec{\phi}^L(r_n)}{dr_n}$ at each of the mesh points in the outward integration region, $r_{n_1} < r_n < r_m$, and the inward integration region, $r_m < r_n < r_{n_2}$. At the mesh

point corresponding to r_m , two values of both functions can be calculated:

$$\frac{d\vec{\phi}_{(1)}^L(r_m)}{dr_n} \quad \text{and} \quad \frac{d\vec{\phi}_{(2)}^L(r_m)}{dr_n}, \text{ corresponding to values obtained from outward}$$

and inward integration, respectively, and the similar pair $\vec{\phi}_{(1)}^L(r_n)$ and $\vec{\phi}_{(2)}^L(r_m)$.

By assumption, the calculated values of $\vec{\phi}_{(1)}^L(r_m)$ and $\vec{\phi}_{(2)}^L(r_m)$ should be the same; a comparison of their elements gives one an estimate of the accuracy which the matrix solution for $\vec{x}_{j_1}$ and the linear superposition of complementary functions are able to obtain.

One may use the discontinuity in $\frac{d\vec{\phi}(r_m)}{dr_n}$ in the more general form

of the Hartree corrector worked out by Cohen, Judd, and Riddell (1960a) to correct the estimate of the total energy eigenvalue E:

$$\delta E = \epsilon \cdot \frac{\sum_j (2 - \delta_{j,0}) [y_j^{(1)}(r_m)]^2 \cdot \left\{ \frac{y_j^{(1)}(r_m)}{y_j^{(1)}(r_m)} - \frac{y_j^{(2)}(r_m)}{y_j^{(2)}(r_n)} \right\}}{\sum_j (2 - \delta_{j,0}) \left\{ \int_0^{r_n} [y_j^{(1)}(r_n)]^2 dr_n + \int_{r_m}^{\infty} [y_j^{(2)}(r_n)]^2 dr_n \right\}}, \quad (3.69)$$

where

$$y_j^{(1)}(r_n) = j\text{-th element of } \vec{\phi}^L(r_n), \quad 0 \leq r_n \leq r_m,$$

$$y_j^{(2)}(r_n) = j\text{-th element of } \vec{\phi}^L(r_n), \quad r_m \leq r_n < \infty,$$

and the prime (') denotes $\frac{d}{dr_n}$.

The largest contribution to the numerator of the above correction δE should come from the term for $j=j_1$, because the other terms ($j \neq j_1$) in principle have been made to have no discontinuity of the logarithmic derivative. Numerically, the terms other than $j=j_1$ will ordinarily be non-zero.

In practice, it is advantageous to put the discontinuity in the element having the largest absolute value. For the cases studied in the present work, the largest element was the first, corresponding to the $\phi_j(r_n)$ associated with the $1s\sigma_g$ electronic state; thus, the energy correction and normalization integral were calculated using the case $j_1=1s\sigma_g$.

Having obtained the energy correction, in principle one may, using the corrected energy, iterate through the initialization procedure, the numerical

solutions of the differential equations, and the joining procedure to obtain a new energy correction. This process may be repeated until the energy correction satisfies some convergence criteria, such as $|\frac{\delta E}{E}| \leq 10^{-7}$.

The rapid growth of elements $\phi_{j \neq 1s\sigma_g, i}(r_n)$ in outward integration of a coupled vector may lead to linear dependency of the complementary solutions $\phi_i^L(r_m)$. This growth tends to be exponential, $e^{k_j x}$, where $k_j = \sqrt{|V_j - E|/\epsilon}$, such that $\phi_{j,i}$ of the highest electronic state having appreciable coupling to $1s\sigma_g$ grows most rapidly, falsely dominating the complementary vectors at the match point. A similar situation is obtained on inward integration. For this reason, two or three iterations were made at an estimate of the energy E to obtain linearly independent complementary vectors. The procedure is outlined below:

One iteration was effected at the initial estimate of the energy E , using the initialization procedure, the numerical solutions of the differential equations, and the joining procedure described above. The joining procedure was done for $j_1=1, 2, \dots, N$, and a dummy energy correction was calculated for $j_1=1$. The values of the elements of $\vec{\phi}^L(r_{n_1})$, $\vec{\phi}^L(r_{n_2})$, and their derivatives were calculated for all the cases $j_1=1, 2, \dots, N$; and another iteration at the original estimate of the energy was effected using these initial values, rather than those of the initialization procedure. Comparison of the values of $\vec{\phi}_{(1)}^L(r_m)$ and $\vec{\phi}_{(2)}^L(r_m)$ calculated from this second or further iteration usually revealed better agreement than the previous iteration had obtained. The energy was then corrected; and two (or more) iterations at each corrected energy were done, until the correction was small enough to satisfy the convergence criteria.

Once the numerical solution had converged to an energy eigenvalue corresponding to a certain vibrational state v , the radial wave function $\phi(r_n)^{v,L,K}$ was normalized by requiring

$$\sum_{j=1}^N (2-\delta_{K_j,0}) \int_{r_n=0}^{\infty} [\phi_j^{v,L,K_j}(r_n)]^2 dr_n = 1, \quad (3.70)$$

where $\phi_j^{v,L,K}(r_n)$ symbolizes the j -th element of $\phi^{v,L,K}(r_n)$. Equation (3.70) is to be compared to Equation (2.60). The summation $\sum_{j=1}^N$ in Equation (3.70) is understood to cover all elements of the coupled vector, replacing the double sum $\sum_K \sum_j$ of Equation (2.60).

VI. CALCULATION OF PHYSICAL QUANTITIES

The expectation value of the internuclear separation r_n and that of its square r_n^2 are of interest because they can be compared with the results of other workers. Consider $\langle v,L,M=0 | r_n^q | v,L,M=0 \rangle$, where $q=1$ or 2 and v labels the vibrational quantum number, $v=0, 1, \dots$.

$$\begin{aligned} \langle v,L,0 | r_n^q | v,L,0 \rangle &= \int d^3 r_n \int d^3 R_u \psi_0^{v,L*} r_n \psi_0^{v,L} \\ &= (N_L)^2 \cdot \int d^3 r_n \int d^3 R_u \left(\sum_K A_{LK} P_L^K \sum_j \frac{\phi_j^{vLK}}{r_n} \psi_{jK} \right)^* \left(\sum_{K'} A_{LK'} P_L^{K'} \right. \\ &\quad \cdot \left. \sum_i \frac{\phi_i^{vLK'}}{r_n} \psi_{iK'} \right) = (N_L)^2 \sum_K \sum_{K'} A_{LK} A_{LK'} \int d^3 r_n P_L^K P_L^{K'} \end{aligned}$$

$$= \sum_j \sum_i \cdot \frac{\phi_j^{\nu L K}}{r_n} \cdot r_n^q \cdot \frac{\phi_i^{\nu L K}}{r_n} \int_{R_\mu} d^3 R_\mu \psi_{jK} \psi_{iK}$$

Using

$$\int_{R_\mu} d^3 R_\mu \psi_{jK} \psi_{iK} = \delta_{j,i} \delta_{K,K}, \int_0^{2\pi} d\phi_n = 2\pi, \text{ and } \int_{\theta_n=0}^{\pi} [P_L^K(\cos \theta_n)]^2 \sin \theta_n d\theta_n = \frac{2}{2L+1} \cdot \frac{(L+K)!}{(L-K)!},$$

one has

$$\begin{aligned} \langle \nu, L, 0 | r_n^q | \nu, L, 0 \rangle &= (N_L)^2 \sum_K [2-\delta_{K,0}] \left[\frac{(L-K)!}{(L+K)!} \right] \cdot (2\pi) \cdot \left[\frac{2}{2L+1} \right. \\ &\cdot \left. \frac{(L+K)!}{(L-K)!} \right] \sum_j \int_0^\infty dr_n r_n^q [\phi_j^{\nu L K}]^2 = \frac{2L+1}{2} \cdot \frac{2}{2L+1} \sum_K [2-\delta_{K,0}] \\ &\cdot \sum_j \int_0^\infty dr_n r_n^q [\phi_j^{\nu L K}]^2 = \sum_K [2-\delta_{K,0}] \sum_j \int_0^\infty dr_n r_n^q [\phi_j^{\nu L K}]^2 \\ &= \int dr_n r_n^q \sum_K [2-\delta_{K,0}] \sum_j [\phi_j^{\nu L K}]^2 \end{aligned} \quad (3.71)$$

These quantities, $\langle r_n \rangle$ and $\langle r_n^2 \rangle$, were calculated by repeated application on the five-point Newton-Coates integration formula (Hildebrand, 1956) at each set of four new mesh points.

The muon-proton overlap γ is directly related to the analysis of experiments on muon capture in hydrogen (Halpern, 1964). The overlap is defined in units of the 1s atomic proton-muon overlap, $\frac{1}{\pi a_{p\mu}^3}$, where $a_{p\mu}$ is

the Bohr radius of the proton-muon atom:

$$a_{p\mu} = \frac{\hbar^2}{M_{p\mu} e^2}, \quad (3.72)$$

where

$$M_{p\mu} = \frac{m_p m_\mu}{m_p + m_\mu}. \quad (3.73)$$

Defining the probability density at a nucleus for a normalized function as

$$P_{\text{rob}}^{\nu, L}(\xi=1, \eta=1, \phi=0) = \int_{r_n} d^3 r_n \int_{R_\mu} d^3 R_\mu \delta(\vec{R}_\mu - \frac{\vec{r}_n}{2}) \cdot |\psi_0^{\nu, L}(r_n, \theta_n, \xi, \eta, \phi)|^2, \quad (3.74)$$

where

$$\delta(\vec{R}_\mu - \frac{\vec{r}_n}{2}) = \frac{\delta(\xi-1) \delta(\eta-1) \delta(\phi_\mu)}{\frac{r_n^3}{8} (\xi^2 - \eta^2)} \quad (3.75)$$

and the units of P_{rob} for the three-body system are $\frac{1}{a_\mu^3}$, see page 10, one has

$$\begin{aligned} P_{\text{rob}}^{\nu, L}(1, 1, 0) &= \int_{r_n} d^3 r_n |\psi_0^{\nu, L}(r_n, \theta_n, \xi=1, \eta=1, \phi=0)|^2 = \int_0^\infty r_n^2 dr_n \cdot \\ &\cdot \int_{\theta_n=0}^\pi d(\cos \theta_n) \int_{\phi_n=0}^{2\pi} d\phi_n N_L^2 \sum_K \sum_{K'} A_{LK} A_{LK'} P_L^K(\cos \theta_n) \cdot \\ &\cdot P_L^{K'}(\cos \theta_n) \cdot \sum_j \sum_i \frac{\phi_j^{\nu LK}(r_n)}{r_n} \cdot \frac{\phi_i^{\nu LK'}(r_n)}{r_n} \cdot \psi_j^K(\xi=1, \eta=1, \phi=0; r_n) \cdot \\ &\cdot \psi_i^{K'}(\xi=1, \eta=1, \phi=0; r_n). \end{aligned} \quad (3.76)$$

Note that the electronic function has the following components:

from Equation (2.36),

$$\rho_K^{\tau\phi}(0) = \begin{cases} 1 \delta_{\tau\phi,c} & , K = 0 , \\ \sqrt{2} \delta_{\tau\phi,c} & , K \neq 0 ; \end{cases} \quad (3.77)$$

from Equation (2.37),

$$M_{jK}(\eta=1, r_n) = \sum_{n=0,1}^{\infty} f_n^{(j)}(r_n) p_{K+n}^K(\eta=1) , \quad (3.78)$$

where

$$p_{K+n}^K(\eta=1) = \delta_{K,0} ; \quad (3.79)$$

and, from Equations (2.38) and (2.39),

$$\Lambda_{j,K=0}(\xi=1, r_n) = (2)^{\sigma_j(r_n)} e^{-P_j(r_n)} g_0^{(j)}(r_n) . \quad (3.80)$$

One defines the electronic probability amplitude at a nucleus as

$$Y_{jK}(\xi=1, \eta=1, \phi=0; r_n) = \eta_j(r_n) \cdot \Lambda_{j0}(1, r_n) \cdot M_{j0}(1, r_n) \cdot \delta_{K,0} \delta_{\tau\phi,c} . \quad (3.81)$$

Then,

$$\begin{aligned} P_{\text{rob}}^{v,L}(1,1,0) &= 2\pi N_L^2 \sum_K \sum_{K'} A_{LK} A_{LK'} \delta_{K,0} \delta_{K',0} \int_{-1}^1 P_L^K(x) P_L^{K'}(x) dx \cdot \\ &\cdot \delta_{\tau\phi,c} [\delta_{K',0} + \sqrt{2}(1-\delta_{K',0})] [\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})] \cdot \int_0^\infty dr_n \sum_j \cdot \\ &\cdot \sum_i \phi_j^{LK} Y_{jK}^L \phi_i^{LK'} Y_{iK'}^L = \delta_{\tau\phi,c} \cdot \sum_K \delta_{K,0} \int_0^\infty dr_n \left\{ \sum_j \phi_j^{LK} Y_{jK} \right\}^2 . \end{aligned}$$

Finally, one may obtain

$$P_{\text{rob}}^{\nu, L}(1, 1, 0) = \delta_{\tau_{\phi, c}} \int_0^{\infty} dr_n \sum_K \delta_{K, 0} \left\{ \sum_j \phi_j^{LK} Y_{j0} \right\}^2, \quad (3.82)$$

because the summation and integration commute.

In the above, one has found that only the electronic states having an electronic magnetic quantum number $K=0$ can give rise to a finite probability density at a nucleus. The quantity $P_{\text{rob}}^{\nu, L}$ was calculated by repeated application of the five-point Newton-Coates integration formula, in a manner similar to the calculation of $\langle r_n \rangle$ and $\langle r_n^2 \rangle$.

The muon-proton overlap γ is obtained from $P_{\text{rob}}^{\nu, L}$:

$$\gamma = \frac{P_{\text{rob}} \cdot \left(\frac{1}{3}\right) \frac{1}{a_{\mu}}}{\frac{1}{\pi} \cdot \left(\frac{1}{3}\right) \frac{1}{a_{p\mu}}} = \pi \cdot \left(\frac{a_{p\mu}}{a_{\mu}}\right)^3 \cdot P_{\text{rob}}, \quad (3.83)$$

where

$$\frac{a_{p\mu}}{a_{\mu}} = \frac{1 + \frac{m_{\mu}}{m_p}}{1 + \frac{m_{\mu}}{2m_p}} \quad (3.84)$$

and the mass m_p is understood to stand for the mass of any single nucleus.

The quantity 2γ is often quoted because the probability density at the nucleus for which $n=-1$ involves the same factors except for the associated Legendre function:

$$P_{K+n}^K(\eta=-1) = (-1)^{K+n} \cdot \delta_{K,0} = (-1)^n \delta_{K,0} \quad (3.85)$$

Since K must equal zero, the summation index n has either all even or all odd values according to whether the electronic state with magnetic quantum number zero is gerade or ungerade; therefore, one has

$$Y_{j0}(\xi=1, \eta=-1, \phi=0; r_n) = (-1)^{(1-\delta_{\pi_{\mu}, g})} Y_{i0}(\xi=1, \eta=1, \phi=0; r_n). \quad (3.86)$$

Thus,

$$P_{rob}^L(1, -1, 0) = (-1)^{2(1-\delta_{\pi_{\mu}, g})} P_{rob}^L(1, 1, 0) = P_{rob}^L(1, 1, 0); \quad (3.87)$$

and the total muon-proton overlap is 2γ .

The electric quadrupole moment is defined (Landau & Lipschitz, 1958,

$$Q_0 = D_0/Ze) \text{ as the quantity } Q_0 = Q_{z,z} = \langle J, J_z=J | \frac{3z^2 - R_{\mu}^2}{2} | J, J_z=J \rangle.$$

One defines

$$Q_{M=0}^{v,L} = \langle v, L, 0 | \frac{3z^2 - R_{\mu}^2}{2} | v, L, 0 \rangle, \quad (3.88)$$

where, from Equations (A.14) and (A.15) in the equal-mass case,

$$z = -\frac{r_n}{2} \cdot \xi \cdot \eta \quad (3.89)$$

and

$$R_{\mu} = \frac{r_{\mu 2}}{2} (\xi^2 + \eta^2 - 1)^{1/2}. \quad (3.90)$$

One thus obtains

$$\begin{aligned}
 Q_0^{\nu,L} &= \int_{\mathbf{r}_n} d^3\mathbf{r}_n \int_{R_\mu} d^3R_\mu (\Psi_0^{\nu,L})^* \cdot \left[\frac{r_n^2}{8} (3\xi^2\eta^2 - \xi^2 - \eta^2 + 1) \right] \cdot \Psi_0^{\nu,L} \\
 &= (N_L)^2 \int_{\mathbf{r}_n} d^3\mathbf{r}_n \cdot \frac{r_n^2}{8} \int_{R_\mu} d^3R_\mu \left(\sum_K A_{LK} P_L^K \sum_j \frac{\phi_j^{\nu,L,K}}{r_n} \psi_{jK} \right) \\
 &\quad \cdot (3\xi^2\eta^2 - \xi^2 - \eta^2 + 1) \left(\sum_{K'} A_{LK'} P_L^{K'} \sum_i \frac{\phi_i^{\nu,L,K'}}{r_n} \psi_{iK'} \right) = (N_L^2) \\
 &\quad \cdot \sum_K \sum_{K'} A_{LK} A_{LK'} \cdot \int_0^{2\pi} d\phi_n \int_{-1}^1 dx P_L^K P_L^{K'} \sum_j \sum_i \int_0^\infty dr_n \frac{r_n^2}{8} \phi_j^{\nu,L,K} \\
 &\quad \cdot \phi_i^{\nu,L,K'} \cdot \left\{ \frac{r_n^3}{8} \int_{\xi=1}^\infty d\xi \int_{\eta=-1}^1 d\eta (\xi^2 - \eta^2) (3\xi^2\eta^2 - \xi^2 - \eta^2 + 1) F_{jK} \right. \\
 &\quad \cdot F_{iK'} \cdot 2\pi \delta_{K,K'} \left. \right\} , \tag{3.91}
 \end{aligned}$$

where one has used the orthogonality of the functions $\rho_K^\tau(\phi)$ and $\rho_{K'}^\tau(\phi)$ in the electronic functions. Noting that

$$\int_0^{2\pi} d\phi_n = 2\pi, \quad \int_{-1}^1 dx P_L^K(x) P_L^K(x) = \frac{2}{2L+1} \cdot \frac{(L+K)!}{(L-K)!}, \text{ and}$$

$$A_{LK} = [\delta_{K,0} + \sqrt{2}(1-\delta_{K,0})] \sqrt{\frac{(L-K)!}{(L+K)!}} \quad (\text{Equation 2.40}), \text{ one obtains}$$

$$\begin{aligned}
 Q_0^{\nu,L} &= \sum_K [2-\delta_{K,0}] \sum_j \sum_i \int_0^\infty dr_n \phi_j^{\nu,L,K}(r_n) \cdot \phi_i^{\nu,L,K}(r_n) \\
 &\quad \cdot Q_{jK,iK}^{el}(r_n) , \tag{3.92}
 \end{aligned}$$

where the matrix element for clamped nuclei is

$$\begin{aligned}
 Q_{jK,iK}^{el}(r_n) &= \frac{r_n^2}{8} \int_{R_\mu} d^3R_\mu (3\xi^2\eta^2 - \xi^2 - \eta^2 + 1) \psi_{jK} \psi_{iK} = \\
 &= \frac{r_n^2}{8} \left\{ \int_{R_\mu} d^3R_\mu (3\xi^2\eta^2 - \xi^2 - \eta^2) \psi_{jK} \psi_{iK} + \delta_{ji} \right\} . \quad (3.93)
 \end{aligned}$$

In the Born-Oppenheimer approximation or the adiabatic approximation one needs calculate only the diagonal matrix element $Q_{j0,j0}^{el}(r_n)$, where $j0$ is the electronic state which has been included:

$$Q_{j0,j0}^{el}(r_n) = \frac{r_n^2}{8} \left\{ \int_{R_\mu} d^3R_\mu (3\xi^2\eta^2 - \xi^2 - \eta^2) [\psi_{j0}]^2 + 1 \right\} \quad (3.94)$$

and

$$Q_{0,adia.}^{v,L} = \int_0^\infty dr_n [\phi_j^{v,L,0}(r_n)]^2 \cdot Q_{j0,j0}^{el}(r_n) . \quad (3.95)$$

The quadrupole moment was calculated only in the adiabatic approximation because all of the integrals required for the electronic matrix elements were not needed to calculate the coupling parameters. Considerable machine time would be expended to calculate the remaining electronic matrix elements.

CHAPTER IV

RESULTS AND DISCUSSION

The electronic states and the coupling parameters are independent of the mass ratio in the homonuclear case. Since these functions are basic to any of the $(H_\mu H)^+$ ions considered, they are discussed first. Subsequent sections then consider the nuclear vibrational-rotational states, considering convergence of the physical quantities as a function the number of electronic states included in the basis. In addition, the effect of the mass ratio on these quantities is examined for the nuclear vibrational-rotational states.

I. RESULTS FOR ELECTRONIC STATES

For the case of total orbital angular momentum $L = 0$ the six electronic states used were $1s\sigma_g$, $2s\sigma_g$, $3s\sigma_g$, $3d\sigma_g$, $4s\sigma_g$, and $4d\sigma_g$. No difficulty was experienced in obtaining the parameters $p_i(r_n)$, $A_i(r_n)$, $\sigma_i(r_n)$, and $W_i(r_n)$ and the coefficients $f_n^{(i)}(r_n)$ and $g_t^{(i)}(r_n)$ on the interval $0.05 \leq r_n \leq 20.00 a_\mu$, so long as one took account of the numerical instability of the continued fractions noted above. Numerical differentiation of all the above functions except $A_i(r_n)$ and $W_i(r_n)$ was necessary, along with numerical differentiation of the normalization constant $\mathcal{N}_i(r_n)$.

The six electronic states used for the case $L = 1$ were $1s\sigma_g$, $2s\sigma_g$, $3s\sigma_g$, $3d\sigma_g$, $3d\pi_g$, and $4d\pi_g$. Note that the last two states have the electronic

magnetic quantum number $m_i = K' = 1$ and that the first four electronic states are the same as those used for $L = 0$. The dominant electronic state is the $1s\sigma_g$ state, and it is the only state needed in the Born-Oppenheimer or adiabatic approximation. Including the Π -states constitutes a higher order correction which conserves the projection of $\vec{L}$ on the laboratory z-axis. No difficulty was experienced in obtaining the parameters and coefficients for $3d\Pi_g$ and $4d\Pi_g$.

The above calculations were done in single-precision (approximately 8 significant figures); and the electronic parameters were obtained with about seven significant figures. The expansion coefficients were thus obtained to an accuracy that was about $1 \cdot 10^{-7}$ times the largest coefficient for either series. Thus, there are about 3 significant figures in a coefficient that is $0(10^{-4})$ times the largest coefficient in that series. The numerical differentiation was performed dropping terms of $0(\overline{\Delta r_n}^4) = 10^{-5}$. It was found that keeping higher order terms tended to introduce numerical instability in differentiation.

Exploratory calculations indicate that double-precision calculation (approximately 16 significant figures) of the parameters and coefficients would be necessary for consideration of higher electronic states such as $5g\sigma_g$ for larger values of r_n , $10a_\mu < r_n < 20a_\mu$. This difficulty arises because the parameters change by less than the eighth significant figure available in single precision for an increment $\Delta r_n = 0.05a_\mu$. A larger increment Δr_n would alleviate part of this difficulty.

Comparison of the potential $V_{1s\sigma_g}(r_n) = \frac{2}{r_n} + W_{1s\sigma_g}(r_n)$ with the quantity $W_{+CJR}(r_n)$ of Cohen, Judd, and Riddell (1959) indicates that $V_{1s\sigma_g}(r_n)$ is lower (more negative) by more than $0(10^{-4})$ than that of Cohen, Judd, and Riddell (1959) for the intervals $r_n < 0.5a_\mu$ and $4 < r_n < 8a_\mu$. For the intervals $0.5 < r_n < 4a_\mu$ and $8 < r_n < 13a_\mu$, $V_{1s\sigma_g}(r_n)$ is lower than $W_{+CJR}(r_n)$ by more than $0(10^{-5})$. In the region of large r_n , $13a_\mu < r_n < 20a_\mu$, there is little difference between the two functions, $V_{1s\sigma_g}(r_n)$ being lower than $W_{+CJR}(r_n)$ by $0(10^{-5})$.

The values of the electronic energies $W_j(r_n)$ agree very well, within $0(10^{-5})$, with those calculated by Bates, Ledsham, and Stewart (1953) to five significant figures. The values of $W_j(r_n)$ used here are expected to be accurate to $0(10^{-7})$ and include some electronic states not calculated by Bates, Ledsham, and Stewart (1953).

The potential $V_j(r_n) = \frac{2}{r_n} + W_j(r_n)$, Equation (2.66), is plotted as a function of the internuclear separation r_n in Figure 3, page 119, for the six electronic states included in the basis for $L = 0$. This potential includes the internuclear repulsion $2/r_n$. A similar plot of $V_j(r_n)$ for the six electronic states included in the basis for $L = 1$ is presented in Figure 4, page 120. Note that $V_j(r_n)$ does not include the nuclear centrifugal barrier term $(L(L+1) - K_j^2)/r_n^2$, cf. Equation (2.190). Four of the electronic states for $L = 1$ are the same as those for $L = 0$.

FIGURE 3

POTENTIAL VERSUS SEPARATION, FOR $L = 0$ BASIS STATES

FIGURE 4

POTENTIAL VERSUS SEPARATION, FOR $L = 1$ BASIS STATES

The electronic probability amplitude at a nucleus $Y_{jk}(\xi=1, \eta=1, \phi=0; r_n)$, Equation (3.81), is illustrated in Figure 5, page 122. This amplitude is identically zero for the two Π -states ($K = 1$) used in the basis for $L = 1$. The electronic s-states ($1s\sigma_g$, $2s\sigma_g$, etc.) approach the probability amplitude of a single-charged helium ion at small internuclear separations. The amplitude of the electronic d-states ($3d\sigma_g$ and $4d\sigma_g$) vanishes at small internuclear separations because of the electronic centrifugal barrier. The asymptotic values correspond to the separated-atoms configuration.

The electronic quadrupole moment of the $1s\sigma_g$ state, $Q_{1s\sigma_g, 1s\sigma_g}^{el}(r_n)$ (Equation 3.94), is plotted in Figure 6, page 123, as a function of the internuclear separation. This function is used below to calculate the quadrupole moment in the adiabatic approximation, by multiplying $Q_{1s\sigma_g, 1s\sigma_g}^{el}(r_n)$ by the radial wave function $\phi_{1s\sigma_g}(r_n)$ and integrating with respect to r_n .

The electric quadrupole moment matrix elements of the higher electronic states were not calculated. The off-diagonal matrix elements require evaluation of certain integrals that do not occur in evaluation of the coupling parameters. Because these integrations require a proportionately large amount of computer time, the higher quadrupole matrix elements were omitted. For systems such as $(\text{pep})^+$ the contribution of these terms to the total electric quadrupole moment is expected to be small.

FIGURE 5

ELECTRONIC PROBABILITY AMPLITUDE FOR μ -p
OVERLAP VERSUS SEPARATION

FIGURE 6

ELECTRONIC QUADRUPOLE MOMENT OF STATE
 $1s_g$ VERSUS SEPARATION

II. RESULTS FOR COUPLING PARAMETERS

The simplest case is that with total orbital angular momentum $L = 0$, which requires only the coupling parameters $g_{jo,io}^{(1)}(r_n)$, $R_{jo,io}(r_n)$, and $\frac{dR_{jo,io}(r_n)}{dr_n}$, where $j \rightarrow n_j, \ell_j$, and $i \rightarrow n_i, \ell_i$. This case involves electronic states with magnetic quantum number $K = K' = 0$, the σ -configuration in the united-atom designation, which have even values of ℓ_j and ℓ_i .

It was found that the positive-definite diagonal coupling parameter $g_{jo,io}^{(1)}(r_n)$ tended toward numerical instability at small values of r_n . This tendency became more pronounced for those higher electronic states having small values of the electronic angular momentum ℓ_j . For example, the coupling parameter $g_{4s\sigma_g, 4s\sigma_g}^{(1)}(r_n)$ showed instability for $r_n < 0.70a_u$, as compared to $g_{4d\sigma_g, 4d\sigma_g}^{(1)}(r_n)$, which showed instability for $r_n < 0.15a_u$.

By use of the significance arithmetic techniques of Burrus and Rust (1966), the instability was traced to cancellation of leading significant digits during the numerical integration processes and the subsequent combination of the integrals to form the parameter. The dominant coefficients in the expansion of $\Lambda_{jm_j}(\xi, r_n)$ for the higher s-states tended to have the sum of zero as $\xi \rightarrow \infty$, resulting in inaccurate values of the integrands. These difficulties could be partially overcome by using double-precision calculation to evaluate the coefficients.

Comparison of the values of $g_{1s\sigma_g, 1s\sigma_g}^{(1)}(r_n)$ to $g_{++CJR}(r_n)$ of Cohen, Judd, and Riddell (1959) indicates that there is good agreement, about two significant figures for $r_n < 4a_\mu$ and about three significant figures for $4 < r_n < 20a_\mu$. The value of this parameter is $0(10^{-1})$ and $g_{1s\sigma_g, 1s\sigma_g}^{(1)}(r_n)$ is larger than $g_{++CJR}(r_n)$ by $0(10^{-3})$ for $r_n < 4a_\mu$. The former is smaller by $0(10^{-4})$ for $5 < r_n < 20a_\mu$. Thus, the effect of this term, multiplied by the mass ratio ϵ , in an effective potential for the important region $r_n < 4a_\mu$ is slightly more repulsive in the present calculation than in that of Cohen, Judd, and Riddell. This effective repulsion partially cancels the lower electronic energy $W_{1s\sigma_g}(r_n)$ used in the present work, but it is felt to be more accurate.

The instability of off-diagonal coupling parameters is enhanced by the fact that the integrands for these parameters are not positive-definite. The tendency toward numerical instability noted for the diagonal coupling parameter $g_{j_0, j_0}^{(1)}(r_n)$ occurred for those off-diagonal parameters $g_{j_0, i_0}^{(1)}(r_n)$ and $Q_{j_0, i_0}(r_n)$ involving a state that had been unstable in its diagonal element. For example, $g_{2s\sigma_g, 4s\sigma_g}^{(1)}(r_n)$ became unstable for $r_n < 0.6a_\mu$, reflecting the instability arising from the $4s\sigma_g$ state on that interval. For $0 < r_n < 10a_\mu$ the parameter $Q_{j_0, i_0}(r_n)$ coupling two higher s-states, for example $Q_{2s\sigma_g, 4s\sigma_g}(r_n)$, showed numerical instability. Numerical

differentiation of this parameter to yield, say, $dQ_{2s\sigma_g, 4s\sigma_g}(r_n)/dr_n$ magnified the instability and caused the coupling coefficient $a_{2s\sigma_g, 4s\sigma_g}(r_n)$ to show considerable scatter for $r_n < 10a_\mu$. The effect of this scatter on the final radial wave function is expected to be small, because the coupling is off-diagonal and does not involve the radial element $\phi_{1s\sigma_g}(r_n)$.

Outside the regions of instability, the coupling parameters $g_{jo,io}^{(1)}(r_n)$ and $Q_{jo,io}(r_n)$ are probably accurate to about three significant figures. Consequently, the coupling parameter $\frac{dQ_{jo,io}(r_n)dr_n}{dr_n}$ is probably accurate to only two significant figures, since it must be obtained by numerical differentiation of $Q_{jo,io}(r_n)$. This accuracy is adequate to the solution of the coupled equations, due to the magnitude of the non-dominant elements of the solution vector $\vec{\phi}(r_n)$.

In the region of instability, $r_n < 0.7a_\mu$, approximate values of the unstable parameters were obtained by graphical extrapolation from the stable region and smoothing such that they paralleled the stable parameter used as a prototype. For example, the stable parameter $g_{1s\sigma_g, 2s\sigma_g}^{(1,1)}(r_n)$ was used as the prototype for $g_{2s\sigma_g, 4s\sigma_g}^{(1,1)}(r_n)$ for $r_n < 0.6a_\mu$. The effect of this extrapolation on the overall solution is expected to be small because of the small values of the non-dominant elements of the solution vector $\vec{\phi}^{0,0}(r_n)$ in this region.

The case $L = 1$ involves both σ and π electronic configurations, corresponding, respectively, to $K = 0$ and $K = 1$. In addition to the above coupling parameters, $g_{jl;il}^{(1,2)}(r_n)$ and $\mathcal{J}_{jo;il}(r_n)$ are required. The evaluation of these parameters yielded results that tended to have numerical stability characteristics similar to those for $L = 0$. Less scatter occurs for $L = 1$ because the $4s\sigma_g$ state was not included in the basis.

The coupling coefficients $a_{ji}(r_n)$, which multiplies $\phi_i(r_n)$, and $b_{ji}(r_n)$, which multiplies $d\phi_i(r_n)/dr_n$, are plotted below. The $L = 0$ case corresponds to Equation (2.191) and is presented in Figures 7 through 10, pages 128 through 131. The $L = 1$ case corresponds to Equations (2.192) and (2.193) and is presented in Figures 11 through 22, pages 132 through 143. These figures present the coupling matrices $\bar{A}$ or $\bar{B}$ of Equation (2.197), one row per plot, as functions of the internuclear separation r_n .

III. RESULTS FOR ENERGIES, PHYSICAL QUANTITIES, AND RADIAL WAVE FUNCTIONS

Five different molecular ions $(H\mu H)^+$ were considered, each system being homonuclear. In order of decreasing mass ratio they were proton-negative muon-proton, $(p\mu p)^+$; deuteron-negative muon-deuteron, $(d\mu d)^+$; triton-negative muon-triton, $(t\mu t)^+$; positive muon-electron-positive muon, $(\mu e \mu)^+$; and proton-electron-proton, $(pep)^+$. In the following, the net charge of the system will be understood to be plus one and a system will be identified simply by the lower case symbols, as in $p\mu p$ for proton-negative muon-proton, $(p\mu p)^+$.

FIGURE 7

COUPLING COEFFICIENTS $a_{1s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 0$ BASIS STATES

FIGURE 8
 COUPLING COEFFICIENTS $a_{3d\sigma_g, i}$ VERSUS SEPARATION,
 FOR $L = 0$ BASIS STATES

FIGURE 9

COUPLING COEFFICIENTS $b_{1s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 0$ BASIS STATES

FIGURE 10

COUPLING COEFFICIENTS $b_{3d\sigma_g, i}$ VERSUS SEPARATION,
FOR $l_i = 0$ RASTS STATES

FIGURE 11

COUPLING COEFFICIENTS $a_{1s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 12

COUPLING COEFFICIENTS $a_{2s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES .

FIGURE 13

COUPLING COEFFICIENTS $a_{3s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 14

COUPLING COEFFICIENTS $a_{3d\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 15

COUPLING COEFFICIENTS $a_{3d\pi_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 16

COUPLING COEFFICIENTS $a_{4d\pi_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 17

COUPLING COEFFICIENTS $b_{1s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 18

COUPLING COEFFICIENTS $b_{2s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 19

COUPLING COEFFICIENTS $b_{3s\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 20

COUPLING COEFFICIENTS $b_{3d\sigma_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 21

COUPLING COEFFICIENTS $b_{3d\pi_g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

FIGURE 22

COUPLING COEFFICIENTS $b_{4d\pi g, i}$ VERSUS SEPARATION,
FOR $L = 1$ BASIS STATES

The masses used for these particles in the following calculations are given in Table II, page 145. The mass ratios ϵ of the above ions are shown in Table III, page 146, along with the Rydberg for the ion, W_μ , and that of the atom, $W_{p\mu}$, where $W_{p\mu} = M_{p\mu} c^2 \alpha^2 / 2$ and $M_{p\mu} = m_\mu / (1 + m_\mu / m_p)$. The ratio $(-W_{p\mu} / W_\mu)$ represents the upper limit for an eigenvalue of the energy E , because at energies above this value the ion would disassociate into an atom and a free nucleus. The symbols p and μ are understood to represent a nucleus and lepton, respectively, of any of the ions considered in Table III or subsequent tables.

The binding energy B is defined (Wessel and Phillipson, 1964) as the difference between the ground state energy of the atom, $-W_{p\mu}$, and the total energy of the system, EW_μ ,

$$B = -(M_{p\mu} + EM_\mu) c^2 \alpha^2 / 2 ,$$

where $M_\mu = m_\mu / \left(1 + \frac{m_\mu}{2m_p}\right)$, cf. Equation (2.4).

In the following, let the coupled equations of order $N = 0$ be defined as the Born-Oppenheimer approximation, cf. page 93; and let order $N = 1$ be defined as the adiabatic approximation, cf. page 93. Two hydrogen molecular ion systems, $p\mu p$ and $p\mu p$, were selected to demonstrate the effect of, respectively, large and small mass ratios ϵ on the energy eigenvalues and certain physical quantities for $L = 0$.

TABLE II
MASSES OF PARTICLES USED IN CALCULATIONS

Particle	Symbol	Mass (MeV.)
Electron	e	0.511006
Muon	μ	105.659
Proton	p	938.256
Deuteron	d	1875.581
Triton	t	2808.802

TABLE III

MASS RATIO ϵ AND RYDBERG W_μ FOR IONS $(H_\mu H)^+$

Ion	Mass Ratio ϵ	$(H_\mu H)^+$ Rydberg W_μ in eV.	(H_μ) Rydberg $W_{p\mu}$ in eV.	$-\frac{W_{p\mu}}{W_\mu}$
p μ p	$2.132187 \cdot 10^{-1}$	2663.175	2528.399	-0.949393
d μ d	$1.095814 \cdot 10^{-1}$	2736.061	2663.104	-0.973335
t μ t	$7.400044 \cdot 10^{-2}$	2761.084	2710.932	-0.981836
μ e μ	$9.649405 \cdot 10^{-3}$	13.57250	13.53984	-0.997594
p e p	$1.088971 \cdot 10^{-3}$	13.60162	13.59792	-0.999728

The following sections reveal that the corrections to the Born-Oppenheimer approximation had a much greater effect on the energy E for large mass ratios. However, almost no significant difference between the results for order $N = 1$ thru $N = 6$ was noted for pep, which has a small mass ratio. For pup, which has a large mass ratio, the differences between each successive order N were significant.

Born-Oppenheimer and Adiabatic Results

For reference, the Born-Oppenheimer ($N = 0$) results are presented in Table IV, page 148. These results represent the lowest rotational ($L = 0$) and ground vibrational ($v = 0$) state of each ion. The binding energy B is larger for the $(\text{H}\mu\text{H})^+$ ions than for the $(\text{HeH})^+$ systems because the Rydberg is based on the reduced mass of the muon for $(\text{H}\mu\text{H})^+$ and on that of the electron for $(\text{HeH})^+$.

The overlap γ has a minimum near the mass ratio of $\text{t}\mu\text{t}$ for these Born-Oppenheimer cases. The minimum in γ arises from the minimum that occurs in the electronic probability amplitude $Y_{1s\sigma_g}(\xi=1, \eta=1, \phi=0; r_n)$, plotted in Figure 5, page 122. The values of $\langle r_n \rangle$ and $\langle r_n^2 \rangle$ show that the radial wave function $\phi_{1s\sigma_g}(r_n)$ tends to be distributed about a larger $\langle r_n \rangle$ with a larger width, $\sqrt{\langle r_n^2 \rangle - \langle r_n \rangle^2}$, for pup than for $\text{t}\mu\text{t}$. The net contribution to γ is larger for pup because the radial wave function has a greater extent past the minimum of $Y_{1s\sigma_g}(1, 1, 0; r_n)$. On the other

TABLE IV
BORN-OPPENHEIMER (N=0) RESULTS FOR GROUND STATE (L=0, v=0)

Ion	E (W_μ)	B (eV.)	$\langle r_n \rangle$ (a_μ)	$\langle r_n^2 \rangle$ (a_μ^2)	γ ($\pi^{-1} a_{p\mu}^{-3}$)
p μ p	-1.080553	349.302	3.212	11.831	0.6469
d μ d	-1.110859	376.275	2.782	8.572	0.6276
t μ t	-1.125964	379.862	2.617	7.463	0.6248
μ e μ	-1.174757	2.40455	2.200	5.015	0.6377
p e p	-1.194793	2.65320	2.063	4.311	0.6510

hand, the radial wave-function of pep has a small width and is concentrated near $2 \cdot a_\mu$, where the electronic probability amplitude has not reached its minimum value.

The adiabatic ($N = 1$) results are shown in Table V, page 150, for all of the ions considered except for pep. The adiabatic results for pep are discussed separately, because of the large number of vibrational levels. Table V shows all the vibrational levels that were found for pup, d_μd, tut, and μep with $L = 0$ or $L = 1$. The binding energies for $v = 0$ are considerably less than those of the Born-Oppenheimer ($N = 0$) runs in Table IV, page 148. This decrease of binding energy arises from inclusion of the diagonal correction term $a_{1s\sigma_g, 1s\sigma_g}(r_n)$, which was called $g_{++}(r_n)$ by Cohen, Judd, and Riddell (1960a). This term in effect represents a repulsion of magnitude $\epsilon \cdot a_{1s\sigma_g, 1s\sigma_g}(r_n)$ added to the potential function $V_j(r_n)$.

The adiabatic results show slightly smaller values of $\langle r_n \rangle$ and $\langle r_n^2 \rangle$ than the Born-Oppenheimer results. This shift of the radial wave function was sufficient to cause a slight increase in the adiabatic values of γ as compared to the $N = 0$ values for the systems studied. This increase is apparently due to the fact that $a_{1s\sigma_g, 1s\sigma_g}(r_n)$ has a maximum near $r_n = 0.8a_\mu$ and a minimum near $r_n = 2.0a_\mu$, which leads to a slightly larger $\phi_{1s\sigma_g}(r_n)$ in a region of larger $Y_{1s\sigma_g}(1,1,0;r_n)$. The minimum γ

TABLE V

ADIABATIC (N=1) RESULTS FOR L=0 AND 1, $\nu \geq 0$

L	Ion	ν	E (W_μ)	B (eV.)	$\langle r_n \rangle$ (a μ)	$\langle r_{n2}^2 \rangle$ (a μ^2)	γ ($\pi^{-1} a_{p\mu}^{-3}$)	$Q_{0,adia}^{\nu,L}$ (a μ^2)
0	p μ p	0	-1.040008	241.324	3.140	11.254	0.6530	1.892
		0	-1.090653	320.988	2.763	8.441	0.6297	1.279
		1	-0.984679	31.038	5.655	37.013	0.5501	8.196
	t μ t	0	-1.112420	360.554	2.608	7.408	0.6260	1.070
		1	-1.010922	80.308	4.407	22.028	0.5482	4.377
	μ e μ	0	-1.173052	2.38141	2.200	5.013	0.6377	0.632
		1	-1.120286	1.66525	2.638	7.507	0.5941	1.072
		2	-1.076943	1.07698	3.153	10.960	0.5601	1.765
		3	-1.042623	0.61117	3.806	16.116	0.5345	2.926
		4	-1.017420	0.26910	4.750	25.062	0.5166	5.131
		5	-1.002042	0.06037	6.578	47.400	0.5061	10.902
	p e p	0	-1.194602	2.65061	2.063	4.311	0.6510	0.518
1	p μ p	0	-0.984845	94.415	3.948	17.857	0.5859	3.391
		0	-1.054568	222.258	3.098	10.572	0.5827	1.704
	t μ t	0	-1.085595	286.488	2.822	8.645	0.5900	1.299
		1	-0.997021	41.926	4.992	28.277	0.5319	5.934
	μ e μ	0	-1.168644	2.32159	2.225	5.125	0.6314	0.649
		1	-1.116564	1.61472	2.667	7.668	0.5890	1.101
		2	-1.073864	1.03518	3.189	11.202	0.5560	1.815
		3	-1.040180	0.57800	3.855	16.520	0.5314	3.020
		4	-1.015652	0.24510	4.832	25.909	0.5144	5.346
		5	-1.001069	0.04717	6.816	50.814	0.5050	-----
	p e p	0	-1.194071	2.64339	2.066	4.322	0.6502	0.519

for a ground state ($L = 0$, $v = 0$) wave function was obtained for t_{ut} in the adiabatic approximation, as well as in the Born-Oppenheimer approximation.

The calculated adiabatic quadrupole moment $Q_{0,\text{adia}}^{v,L}$, Equation (3.95), is also tabulated in the adiabatic results. The electronic state included in calculation of $Q_{0,\text{adia}}^{v,L}$ was the $1s\sigma_g$ state.

Figure 23, page 152, graphically summarizes the rotational-vibrational energy levels shown in Table V, page 150, as functions of the mass ratio ϵ . The curves shown on this plot are intended to serve as guides from one mass ratio to the next, because the energies at all of the intermediate mass ratios were not calculated. The reader is also referred to Table XI, page 177, for the adiabatic results for pep.

The curve labeled "Top of Well" in Figure 23, page 152, was obtained from the disassociation energy eigenvalue, $-W_{p\mu}/W_{\mu}$, of Table III, page 146. The curve labeled "Bottom of Well" in Figure 23 was obtained from $V_B(r_n) = [V_{\min} + \epsilon : a_{1s\sigma_g, 1s\sigma_g}(r_n \rightarrow \infty)] \cdot W$, where the first term represents the minimum of the potential, $V_{1s\sigma_g}(r_n = 2 a_{\mu}) = -1.205268$, and the second term represents the asymptotic value of the effective repulsion of the lowest order coupling term. The curve labeled "Born-Oppenheimer" was obtained from Table IV, page 148. The other curves of Figure 23 were obtained from Table V, page 150; Table XI, page 177; and Table XII, page 178. The necessity of including corrections to the Born-Oppenheimer approximation for the larger mass ratios is well demonstrated by Figure 23.

FIGURE 23

ROTATIONAL-VIBRATIONAL ENERGY LEVELS VERSUS MASS RATIO

Order-of-magnitude considerations, such as those given in Messiah (1962) on page 782 may be compared to Figure 23, page 152. The kinetic energy T may be estimated from the uncertainty principle

$$\Delta p \cdot \Delta x \approx \hbar,$$

because Δx must be of the order of a_μ . Approximating the spread in the momentum as an estimate of the momentum, one obtains

$$p \approx \frac{\hbar}{a_\mu}$$

and

$$T \approx \frac{p^2}{2M_\mu} = \frac{\hbar^2}{2M_\mu a_\mu^2}.$$

Recall that $a_\mu = \hbar^2/(M_\mu e^2)$ and $W_\mu = M_\mu e^4/(2\hbar^2)$, from which

$$W_\mu = \frac{\hbar^2}{2M_\mu a_\mu^2}.$$

Consequently, the kinetic energy T and the Rydberg W_μ have about the same magnitudes

$$T \approx W_\mu.$$

Because W_μ is the unit of the electronic energy, the kinetic energy and the electronic energy are of the same magnitude. The Rydberg W_μ is tabulated in Table III, page 146.

Considering next the vibrational energy levels, one notes that the potential well of the $1s\sigma_g$ state may be fit approximately by

$$V_{1s\sigma_g}(r_n) \approx V_{\min} + \frac{k \cdot (r_n - 2)^2}{2} \cdot W_\mu,$$

where $k \approx 0.20 \text{ a}_\mu^{-2}$, near the minimum at $r_n = 2 \text{ a}_\mu$. In turn the vibrational energy levels differ by

$$T_{\text{vib}} \approx \hbar\omega$$

in the simple harmonic oscillator model, where

$$\omega = \sqrt{kW_\mu/M_n} = \sqrt{k/(M_n W_\mu)} W_\mu.$$

Thus the spacing of vibrational energy levels is

$$T_{\text{vib}} \approx 0.5 \sqrt{\frac{m_\mu}{m_p}} \cdot W_\mu.$$

For the ions pup , dud , tut , μeu , and pep this vibrational spacing is approximately 450 eV., 300 eV., 250 eV., 0.4 eV., and 0.1 eV., respectively.

The rotational energy levels are given by $J^2/(2I)$, where J is the angular momentum and I is the moment of inertia. The spacing between the rotational levels is expected to arise from a change in J such that $\Delta J = \hbar$, and the moment of inertia is $I \approx 2m_p a_\mu^2$. The spacing between rotational energy levels then becomes

$$T_{\text{rot}} \approx \frac{\hbar^2}{4m_p a_\mu^2} = \frac{M_\mu}{2m_p} \cdot W_\mu \approx \frac{m_\mu}{2m_p} \cdot W_\mu.$$

For the ions pup , dud , tut , $\mu e\mu$, and pep this rotational spacing is approximately 150 eV., 70 eV., 50 eV., 0.03 eV., and 0.004 eV., respectively.

The above order-of-magnitude considerations have led to the conclusion that the kinetic energy has the same magnitude as the electronic energy, the spacing of vibrational levels is less than the electronic energy by $\sqrt{m_\mu/m_p}$, and the spacing of the rotational energy levels is less than the electronic energy by m_μ/m_p . This relationship is summarized by

$$T \approx W_\mu > T_{vib} > T_{rot} \quad .$$

The magnitudes calculated for T_{vib} and T_{rot} compare very well with those of Table V, page 150; Table XI, page 176; and Table XII, page 177.

Convergence of pup for $L = 0$ and 1

The results for pup are presented in Table VI, page 156. For the large mass ratio of pup , $\epsilon = 0.213$, the changes to the energy E due to including each electronic state in the basis are presented in Table VII, page 157. From Table VII it is seen that the effect of including electronic s-states ($\ell_j = 0$) above $2s\sigma_g$ was relatively small. The change of energy due to $4d\sigma_g$ was considerably less than that of $3d\sigma_g$; however, the change due to $3d\sigma_g$ was more than that due to $2s\sigma_g$. The largest changes to the energy, arising from the states included for $L = 0$, were due to the states

TABLE VI
CONVERGENCE OF $p_{\mu p}$ FOR $L=0$ AND 1, $v=0$

L	N	Basis	E	B	$\langle r_n \rangle$	$\langle r_n^2 \rangle$	γ
			(a_μ)	(eV.)	(a_μ)	(a_μ^2)	($\pi^{-1} a_{p\mu}^{-3}$)
0	0	$1s_g$	-1.080553	349.302	3.212	11.831	0.6469
	1	$1s_g$	-1.040008	241.324	3.140	11.254	0.6530
	2	$1s_g, 2s_g$	-1.040707	243.184	3.131	11.186	0.6467
	3	$1s_g, 2s_g, 3s_g$	-1.040818	243.480	3.130	11.174	0.6457
	4	$1s_g, 2s_g, 3s_g, 3d_g$	-1.042433	247.782	3.133	11.180	0.6311
	5	$1s_g, 2s_g, 3s_g, 3d_g, 4s_g$	-1.042472	247.887	3.132	11.175	0.6307
	6	$1s_g, 2s_g, 3s_g, 3d_g, 4s_g, 4d_g$	-1.042738	248.593	3.132	11.168	0.6276
1	0	$1s_g$	-1.028023	209.405	4.148	19.930	0.5813
	1	$1s_g$	-0.984845	94.415	3.948	17.857	0.5859
	2	$1s_g, 2s_g$	-0.985372	95.817	3.935	17.723	0.5807
	3	$1s_g, 2s_g, 3s_g$	-0.985453	96.035	3.933	17.700	0.5798
	4	$1s_g, 2s_g, 3s_g, 3d_g$	-0.987267	100.866	3.921	17.536	0.5618
	5	$1s_g, 2s_g, 3s_g, 3d_g, 3d\pi_g$	-0.987442	101.332	3.922	17.544	0.5620
	6	$1s_g, 2s_g, 3s_g, 3d_g, 3d\pi_g, 4d\pi_g$	-0.987496	101.475	3.922	17.542	0.5620

TABLE VII

CHANGE OF ENERGY, $\Delta E = E_N - E_{N-1}$, AND CHANGE OF OVERLAP, $\Delta\gamma = \gamma_N - \gamma_{N-1}$, FOR $p\mu p$
AS FUNCTIONS OF ELECTRONIC QUANTUM NUMBERS OF BASIS STATE N

L	ℓ_N	m_N	$\Delta E \text{ in } 10^{-4} \cdot W_\mu$			
			n_N			
			1	2	3	4
0	0	0	+405.45	-6.29	- 1.11	-0.39
	2	0			-16.15	-2.66
1	0	0	+431.78	-5.25	- 0.81	
	2	0			-18.14	
	2	1			- 1.75	-0.54
L	ℓ_N	m_N	$\Delta\gamma \text{ in } 10^{-3} \cdot (\pi^{-1} a_{p\mu}^{-3})$			
			n_N			
			1	2	3	4
0	0	0	+ 6.1	-6.3	- 1.0	-0.4
	2	0			-14.6	-3.1
1	0	0	+ 4.6	-5.2	- 0.9	
	2	0			-18.0	
	2	1			+ 0.2	+0.0

$2s\sigma_g$ and $3d\sigma_g$, because these states have potential energies closest to that of $1s\sigma_g$ and give rise to large coupling coefficients.

The data presented in Table VII, page 157, for pup indicate that the overall convergence of the expansion was slow enough with respect to the energy that several more electronic states need to be included in the basis. Significantly, all changes to the energy for order $N > 1$ were negative. With the six states that were included in the basis, it appears that the energy has been determined to $0(10^{-3}W_\mu) = 3 \text{ eV}$. The lowering of the energy due to the states $5g\sigma_g$ and $5d\sigma_g$ would be of special interest, because $5g\sigma_g$ would provide a third term on the diagonal of Table VII and $5d\sigma_g$ would provide a third term in the d-state series of Table VII.

The data of Table VI, page 156, indicate that the changes to $\langle r_n \rangle$ and $\langle r_n^2 \rangle$ due to the higher states were not all of the same sign. The largest change to $\langle r_n \rangle$ and $\langle r_n^2 \rangle$ was due to the $2s\sigma_g$ state. The value of $\langle r_n \rangle$ appears to have converged to $0(10^{-3}a_\mu)$ and that of $\langle r_n^2 \rangle$ to $0(10^{-2}a_\mu^2)$. The changes to the overlap γ of Table VI due to including each electronic state in the basis are also presented in Table VII, page 157. The value of γ decreased for each electronic state above $1s\sigma_g$ that was included in the basis for $L = 0$; thus, the final value is regarded as an upper limit on the overlap. The largest change to the value of γ was due to the $3d\sigma_g$ state for both $L = 0$ and $L = 1$. The electronic Π -states

($m_N = 1$) included in the $L = 1$ basis states increased γ by a small amount; however, the higher σ -states would decrease γ enough that the $N = 6$ result may be regarded as an upper limit for γ . The value of γ has apparently converged to $O(10^{-2})$ for the coupled solution of order $N = 6$.

In summary for pep, the values of the energy E and the overlap γ were the quantities most sensitive to inclusion of higher electronic states for larger mass ratios. The inclusion of six electronic states in the basis was not enough to yield convergence for the interesting quantities to an order commensurate with the accuracy demanded of the electronic wave functions and the electronic energies. Higher electronic states, however, might tend to be numerically unstable in calculation of the coupling parameters $a_{ji}(r_n)$ and $b_{ji}(r_n)$.

Convergence of pep for $L = 0$

For the small ratio of pep, $\epsilon = 1 \cdot 10^{-3}$, the data of Table VIII, page 160, indicate that the energy E was not sensitive to the inclusion of higher electronic states. Apparently, the value of E has been determined to $O(10^{-5} W_e) = O(10^{-4} \text{ eV.})$ for either the adiabatic approximation of order $N = 1$ or the coupled solution of order $N = 6$. Table VIII indicates that $\langle r_n \rangle$ has been determined to $O(10^{-3} a_e)$, and $\langle r_n^2 \rangle$ has been determined to $O(10^{-3} a_e^2)$. The value of the overlap γ has apparently been determined to $O(10^{-4} \pi^{-1} a_{pe}^{-3})$.

TABLE VIII
CONVERGENCE OF pep FOR GROUND STATE (L=0, v=0)

N	Basis	E (W_e)	B (eV.)	$\langle r_n \rangle$ (a_e)	$\langle r_n^2 \rangle$ (a_e^2)	γ ($\Pi^{-1} a_{pe}^{-3}$)
0	1s σ_g	-1.194793	2.65320	2.063	4.311	0.6510
1	1s σ_g	-1.194602	2.65061	2.063	4.310	0.6510
2	1s σ_g , 2s σ_g	-1.194614	2.65077	2.061	4.303	0.6516
3	1s σ_g , 2s σ_g , 3s σ_g	-1.194614	2.65077	2.061	4.303	0.6517
4	1s σ_g , 2s σ_g , 3s σ_g , 3d σ_g	-1.194614	2.65077	2.062	4.306	0.6515
5	1s σ_g , 2s σ_g , 3s σ_g , 3d σ_g , 4s σ_g	-1.194614	2.65077	2.062	4.306	0.6517
6	1s σ_g , 2s σ_g , 3s σ_g , 3d σ_g , 4s σ_g , 4d σ_g	-1.194614	2.65077	2.062	4.306	0.6517

In summary for pep, the energy E and the physical quantities $\langle r_n \rangle$, $\langle r_n^2 \rangle$, and γ were not so sensitive to the higher electronic states as were the similar quantities for pup. It is expected that for most purposes the adiabatic approximation, $N = 1$, will suffice to $O(10^{-5}W_e)$ in E , to $O(10^{-2}a_e)$ in $\langle r_n \rangle$, to $O(10^{-1}a_e^2)$ in $\langle r_n^2 \rangle$, and to $O(10^{-2}\pi^{-1}a_{pe}^{-3})$ in γ .

Radial Wave Functions

More numerical difficulty was experienced in obtaining the coupled solutions of order $N \geq 2$ for pep than for pup. This difficulty was apparently caused by a much greater tendency of the initial complementary solutions to grow exponentially in the direction of integration, see page 107. The net result of the coupling and the exponential growth was that the complementary solutions tended more toward linear dependence at the match point in the first iteration for pep than for pup.

There apparently exists only a very small range of initial values of the elements $\vec{\phi}(r_{n_1})$ or $\vec{\phi}(r_{n_2})$ which avoids introduction of spurious exponential growth in the coupled equations. For pep this range of initial values is less than the approximately eight significant digits available on the IBM 7090 computer, unless $r_{n_1} = 1.4a_\mu$ and $r_{n_2} = 2.9a_\mu$. This range of r_n included approximately 99 per cent of the normalization integral

$$\sum_{j=1}^N (2^{-\delta_{K_j,0}}) \int_{r_n=0}^{\infty} [\phi_j(r_n)]^2 dr_n = 1 ,$$

so that the effect of reducing the integration interval for pep is expected to be small. For pup the values of the limits were $r_{n_1} = 0.25a_\mu$ and $r_{n_2} = 13.9a_\mu$, which included approximately 99.996 per cent of the normalization integral. Consequently, the effect of reducing the integration interval for pup was very small.

The accuracy of the radial wave functions is difficult to determine. Inaccuracy stems largely from the following sources: (1) contributions to the normalization integral from higher elements not included in the coupled equations of order $N = 6$ and from the continuum; (2) the interaction of these higher elements with the six elements included; (3) the reduced integration interval, which affects the initial values of the elements and the estimate of their contributions to the normalization integral; (4) the numerical accuracy of the coupling coefficients and the electronic energies; and (5) the numerical accuracy of the Runge-Kutta-Gill process. It is estimated that the individual elements $\phi_j(r_n)$ for the coupled solution are accurate to $O(10^{-3})$ for pup and for pep. This accuracy would be estimated at $O(10^{-5})$, if the effect of (1) and (2) above on pup were known and the effect of (3) above on pep were known. The effect of (3) could be diminished by performing the solution of the coupled equations in double precision on a computer having larger storage capabilities.

The ortho ($L = 1$) state of pup with $v = 0$ was selected to demonstrate the radial wave functions for an order $N = 6$ solution. The vibrational amplitude $\phi_{1s\sigma_g}(r_n)$ is plotted versus the internuclear separa-

tion r_n in Figure 24, page 164. The corresponding amplitude $\phi_j(r_n)$, $j \neq 1s\sigma_g$, are plotted on a different scale in Figure 25, page 165, because of the smaller magnitudes of these non-dominant elements. In Figure 26, page 166, the product $\phi_j(r_n) \cdot Y_j(\xi=1, \eta=1, \phi=0; r_n)$, $j \neq 1s\sigma_g$, which represents the vibrationally weighted probability amplitude for $\mu - p$ overlap of a non-dominant electronic state j , is plotted versus r_n . Note that this quantity is zero for $3d\pi_g$ and $4d\pi_g$. In Figure 27, page 167, the overlap probability $|\phi_{1s\sigma_g}(r_n) \cdot Y_{1s\sigma_g}(1,1,0;r_n)|^2$ of the dominant state is plotted versus r_n , along with the order $N = 6$ overlap probability $|\sum_j \phi_j(r_n) \cdot Y_j(1,1,0;r_n)|^2$. From Figure 27, it is seen that the net contribution of the non-dominant electronic states to the overlap γ is relatively small.

Effect of Mass Ratio ϵ and Total Orbital Angular Momentum L on Order $N = 6$ Solutions

The results for the total energy E , the binding energy B , the quantities $\langle r_n \rangle$ and $\langle r_n^2 \rangle$, and the overlap γ are presented in Table IX, page 168, for coupled solutions of order $N = 6$. These results were obtained with $L = 0$ and $L = 1$ for various vibrational states, $v \geq 0$. The six electronic basis states for $L = 0$ are given on page 116 and those for $L = 1$ on page 116. There are 10 expansion coefficients for the "inner" function and 10 for the "outer" function of each electronic state in the basis, making 120 expansion coefficients in the basis which may generate 600 cross terms.

FIGURE 24

VIBRATIONAL AMPLITUDE $\Phi_{1\sigma_g}$ VERSUS SEPARATION,
FOR ORTHO ($L = 1$) pwp

FIGURE 25

VIBRATIONAL AMPLITUDE ϕ_j VERSUS SEPARATION,
FOR ORTHO ($L = 1$) $p\mu p$

FIGURE 26

VIBRATIONALLY WEIGHTED PROBABILITY AMPLITUDE $\Phi_j Y_j$
 FOR μ -p OVERLAP IN ELECTRONIC STATE j ,
 FOR ORTHO ($L = 1$) $p\mu p$

FIGURE 27

OVERLAP PROBABILITY VERSUS SEPARATION,
FOR ORTHO ($L = 1$) $p\mu p$

TABLE IX
ORDER N=6 RESULTS FOR L=0 AND 1, $\nu \geq 0$

L	Ion	ν	E (W_μ)	B (eV.)	$\langle r_n \rangle$ (a_μ)	$\langle r_n^2 \rangle$ (a_μ)	γ ($\pi^{-1} a_{p\mu}^{-3}$)
0	p μ p	0	-1.042738	248.593	3.132	11.168	0.6276
	d μ d	0	-1.091534	323.400	2.760	8.421	0.6187
		1	-0.985781	34.053	5.571	35.944	0.5371
	t μ t	0	-1.112872	361.801	2.607	7.399	0.6190
		1	-1.011676	82.391	4.390	21.877	0.5391
	μ e μ	0	-1.173057	2.38148	2.199	5.007	0.6371
	p e p	0	-1.194614	2.65077	2.062	4.306	0.6517
1	p μ p	0	-0.987496	101.475	3.922	17.542	0.5620
	d μ d	0	-1.055415	224.576	3.096	10.544	0.5725
	t μ t	0	-1.086026	287.676	2.820	8.635	0.5838
		1	-0.997657	43.683	4.983	28.324	0.5244
	μ e μ	0	-1.168645	2.32160	2.224	5.118	0.6310
	p e p	0	-1.194082	2.64354	2.065	4.318	0.6507

Comparison of the order $N = 6$ results of Table IX, page 168, with the $N = 1$ (adiabatic) results of Table V, page 150, indicates that the binding energy B is significantly larger for the $N = 6$ results for $p\mu p$, $d\mu d$, and $t\mu t$. For $\mu e\mu$ and $p e p$ the binding energies for $N = 6$ are also larger, but the effect of the higher electronic states in the basis is seen to decrease with decreasing mass ratio.

The values of $\langle r_n \rangle$ and $\langle r_n^2 \rangle$ were slightly smaller for the $N = 6$ results, as compared to the $N = 1$ results. The one exception is $\langle r_n^2 \rangle$ for $t\mu t$ with $L = 1$, $v = 1$ which is $0(10^{-1} a_\mu^2)$ larger for $N = 6$ than for $N = 1$. This fact is an indication that the vibrational states with total energies $|E| < 1$ have such a large extent in the space of r_n that there is less significance in the physical quantities than for the lower vibrational states. The tendency of $v = 0$ radial wave functions $\phi_{1s\sigma_g}(r_n)$ to have a maximum near the minimum of the $V_{1s\sigma_g}(r_n)$ potential at $r_n = 2 a_\mu$ may be observed in the values of $\langle r_n \rangle$ in Table IX, page 168, for $\mu e\mu$ and $p e p$.

The striking results for the overlap γ with Born-Oppenheimer ($N = 0$), adiabatic ($N = 1$), and order $N = 6$ solutions are shown in Figure 28, page 170, as a function of the mass ratio ϵ . The curves drawn in Figure 28 are intended to serve as guides, because γ was not calculated for all mass ratios intermediate to those of Table IX, page 168. For $L = 0$ the Born-Oppenheimer ($N = 0$), adiabatic ($N = 1$), and order $N = 6$ values of γ are plotted. For $L = 1$ the adiabatic and $N = 6$ values of γ are shown.

FIGURE 28

OVERLAP VERSUS MASS RATIO FOR BORN-OPPENHEIMER ($N = 0$),
ADIABATIC ($N = 1$), AND ORDER $N = 6$
RESULTS WITH $\nu = 0$

Figure 28, page 170, reveals that the $N = 6$ values of γ are considerably smaller than the adiabatic values for pup, d_{pd}, and t_{pt}. The $N = 6$ values of γ are slightly larger than the corresponding $N = 1$ values for pep. In the case of pep, the increase in γ may be explained by the decrease in $\langle r_n \rangle$ and $\langle r_n^2 \rangle$, because the radial wave function $\phi_{1\sigma_g}(r_n)$ is shifted toward a region of larger overlap probability amplitude $Y_{1\sigma_g}(1,1,0;r_n)$. In addition, the radial wave functions associated with the higher electronic states, $\phi_j(r_n)$, $j \neq 1\sigma_g$, make a small contribution to the normalization integral for pep, such that the magnitude of $\phi_{1\sigma_g}(r_n)$ is not appreciably decreased.

The decrease in γ for $N = 6$ in the case of pup arises primarily from two effects. The magnitude of the $\phi_{1\sigma_g}(r_n)$ element is slightly less than that in the adiabatic case, because of contributions to the normalization integral from corresponding elements of higher electronic states. Also, contributions to the overlap probability amplitude from the higher electronic states are negative for most of the region of r_n , as may be seen from Figure 26, page 166.

The minimum $N = 6$ value of γ for $L = 0$ was obtained for d_{pd}, rather than for t_{pt}, as was calculated with $N = 0$ and $N = 1$. For $N = 6$ and $L = 1$ the shape of the γ curve in Figure 28, page 170, was altered from that for $N = 1$ sufficiently that no minimum in γ was observed for the mass ratios.

considered. From Table VII, page 157, it may be seen that higher electronic σ -states ($m_N = 0$) may be expected to lower the estimate of γ for $L = 1$ by $O(10^{-2} \pi^{-1} a_{pu}^{-3})$ for pup , but this fact would not radically alter the shape of the $N = 6$, $L = 1$ curve in Figure 28.

The order $N = 6$ results for the binding energy B and overlap γ are compared to the results of other authors in Table X, page 173. The results of Belyaev et al. (1960) using a Morse potential may be expected to give a good approximation to a final result, but these results were not expected by Belyaev et al. (1960) to have very great accuracy. The correspondence of the results of Belyaev et al. (1960) to the present work may be said to be very good.

The adiabatic results of Cohen, Judd, and Riddell (1960b), Weinberg (1960), and Cohen, Hiskes, and Riddell (1960) correspond very well to Becker and Patterson (1964) and to Table V, page 150. The work in the first three papers above is based on variational electronic wave functions of the simple Guillemin-Zener (1929) form for the $1s\sigma_g$ state. The adiabatic calculations yield values for γ which are closer to the present order $N = 6$ results than to those of the variational calculations which are discussed below.

The early variational calculation of Kolos, Roothaan, and Sack (1960) yielded larger binding energies than that of Froman and Kinsey (1961) for pup and dud with $L = 0 = v$. The binding energy obtained by the former authors is slightly larger for pup with $L = 0 = v$ than the

TABLE X
COMPARISON OF PREVIOUS RESULTS TO THE PRESENT WORK
B IN eV., γ IN $\pi^{-1}a_{\mu}^{-3}$

Author(s)	L	ν	pup		dud		tut		pep	
			B	γ	B	γ	B	γ	B	γ
Present Work	0	0	248.6	0.628	323.4	0.619	361.8	0.619	2.651	0.652
	0	1			34.1	0.537	82.4	0.539	2.379	0.634
	1	0	101.5	0.562	224.6	0.573	287.7	0.584	2.644	0.651
	1	1					43.7	0.524	2.372	0.633
Adiabatic:										
Becker and Patterson (1964) ^a	0	0	241.0	0.652	321.0	0.628				
	1	0	94.4	0.586	222.3	0.581				
Cohen, Judd, and Riddell (1960b) ^b	0	0	241	0.654 ^c	322				2.649 ^d	
	1	0	93	0.583 ^c	223					
Morse Potential:										
Belyaev et al. (1960)	0	0	252		330		367			
	0	1			40		86			
	1	0	109		226		288			
	1	1			7(?)		45			
Variational:										
Carter (1966)	0	0	252.4	0.568	324.5	0.585	361.6	0.595		
	0	1			35.1	0.504	75.4	0.516		
Kabir (1966)	1	0	104.9	0.505						
Halpern (1964b)	1	0	107.2	0.505	226.6	0.545	288.7	0.565		
Wessel and Phillipson (1964)	0	0	254.3	0.573						
	1	0	102.2	0.500						
Fröman and Kinsey (1961)	0	0	233		308					
Kolos, Roothaan, and Sack (1960)	0	0	249.6		322.9				2.27	

^aUsed exact electronic wave functions of Bates, Ledsham, and Stewart (1953)

^bUsed variational electronic wave functions of Guillemin-Zener (1929) form

^cWeinberg (1960)

^dCohen, Hiskes, and Riddell (1960)

present work, although the present work yields larger binding for $d\mu d$ and pep with $L = 0 = \nu$ than that of Kolos, Roothaan, and Sack (1960).

Of the recent variational calculations, the largest binding for $L = 0 = \nu$ $p\mu p$ was obtained by Wessel and Phillipson (1964). This value, which is 5.7 eV. larger than the present work, resulted from the variation of an 80-term trial function. The value of γ obtained for this case was smaller by $0.055 \pi^{-1} a_{p\mu}^{-3}$ than that of the present work. Carter (1966) obtained the largest variational binding energies for $d\mu d$ and $t\mu t$ with $L = 0$ and $\nu = 0, 1$ that are listed in Table X, page 173. The results of Carter (1966) for $t\mu t$ with $L = 0$ and $\nu = 0$ is only 0.2 eV. larger than that of the present work, although γ is smaller by $0.024 \pi^{-1} a_{t\mu}^{-3}$ than the present work.

For $t\mu t$ with $L = 0$ and $\nu = 1$, the present work yields a binding energy larger by 7.0 eV. than that of Carter (1966), although the value quoted by Carter (1966) for γ is still $0.023 \pi^{-1} a_{t\mu}^{-3}$ smaller than that of the present work. It is noted that this case, $t\mu t$ with $L = 0$ and $\nu = 1$, is the only one for which the present work obtained a larger binding energy than the best variational calculation for a mesic ion. Further, the value of γ obtained in this case is larger than that of the variational calculation by the same magnitude that was observed in the cases for which the variational calculation yielded larger values of the binding energy.

The largest variational binding energies for $L = 1$ were obtained by Halpern (1964b) using 88 parameters in the trial functions for $p\mu p$, $d\mu d$, and $t\mu t$ with $\nu = 0$. This energy for $p\mu p$ is 2.3 eV. larger than that of

Wessel and Phillipson (1964), although the values of γ obtained by these authors agree within $0.005 \pi^{-1} a_{pu}^{-3}$. The binding energy obtained by Halpern (1964b) is 5.7 eV. larger than that of the present work; however, the value of γ is smaller by $0.057 \pi^{-1} a_{pu}^{-3}$ than that of the present work. The results of Halpern (1964b) for the $L = 1, v = 0$ binding energies of dud and tut are only 2.0 eV. and 1.0 eV. larger, respectively, than those of the present work. The values of γ obtained by Halpern (1964b) in these two cases are $0.028 \pi^{-1} a_{du}^{-3}$ and $0.019 \pi^{-1} a_{tu}^{-3}$ smaller, respectively, than those of the present work.

The value of γ for $L = 1, v = 1$ tut had not been previously calculated, although Belyaev et al. (1960) predicted the existence of this energy level. The $N = 6$ results for pep are essentially the same as the adiabatic ($N = 1$) results which are discussed below.

Higher Vibrational States of pep, H_2^+ , for $L = 0, 1$, and 2

It was noted above that the adiabatic approximation, $N = 1$, suffices to treat the ordinary hydrogen molecular ion pep, H_2^+ , to $O(10^{-5} W_\mu)$ in energy E . Also, the $N = 1$ solution avoids the unknown effect of a reduced interval of integration, r_{n1} to r_{n2} , because the limits can be selected to include practically all of the wave function in this uncoupled case, without requiring a great amount of computation time. Thus, it was elected to run the higher vibrational states of pep in the adiabatic approximation, $N = 1$. These results are presented in Tables XI, XII, and XIII, on pages 176, 177, and 178, respectively.

TABLE XI
ADIABATIC (N=1) RESULTS FOR pep, L=0

L	ν	E	B	$\langle r_n \rangle$	$\langle r_n^2 \rangle$	γ	$Q_{0, \text{adia}}^{\nu, 0}$
		(W _e)	(eV.)	(a _e)	(a _e ²)	($\Pi^{-1} a_{pe}^{-3}$)	(a _e ²)
0	0	-1.19460	2.6506	2.063	4.311	0.651	0.518
	1	-1.17463	2.3789	2.199	4.997	0.634	0.628
	2	-1.15581	2.1230	2.339	5.751	0.618	0.754
	3	-1.13812	1.8823	2.486	6.582	0.604	0.900
	4	-1.12147	1.6559	2.632	7.460	0.591	1.06
	5	-1.10595	1.4448	2.803	8.537	0.578	1.27
	6	-1.09144	1.2475	2.975	9.690	0.567	1.50
	7	-1.07796	1.0641	3.160	10.99	0.556	1.77
	8	-1.06550	0.8945	3.361	12.48	0.547	2.09
	9	-1.05404	0.7388	3.580	14.21	0.538	2.48
	10	-1.04361	0.5969	3.823	16.23	0.531	2.95
	11	-1.03421	0.4690	4.101	18.67	0.523	3.53
	12	-1.02586	0.3554	4.418	21.64	0.517	4.27
	13	-1.01858	0.2564	4.788	25.37	0.513	5.21
	14	-1.01241	0.1723	5.247	30.34	0.509	6.48
	15	-1.00702	0.0992	5.897	38.17	0.51	8.52
	16	-1.00333	0.0490	6.778	49.82	0.51	11.5
	17	-1.00095	0.0166	8.233	72.36	0.50	17.4
	18	-0.99989	0.0022	11.79	146.7	0.50	36.2

TABLE XII
ADIABATIC (N=1) RESULTS FOR pep, L=1

L	ν	E	B	$\langle r_n \rangle$	$\langle r_n^2 \rangle$	γ	$Q_{0, \text{adia}}^{\nu, 1}$
		(w_e)	(eV.)	(a_e)	(a_e^2)	($\pi^{-1} a_{pe}^{-3}$)	(a_e^2)
1	0	-1.19407	2.6434	2.066	4.322	0.650	0.519
	1	-1.17413	2.3721	2.201	5.009	0.633	0.629
	2	-1.15534	2.1165	2.342	5.767	0.617	0.756
	3	-1.13767	1.8762	2.489	6.598	0.603	0.902
	4	-1.12104	1.6501	2.634	7.476	0.590	1.06
	5	-1.10555	1.4394	2.806	8.557	0.577	1.27
	6	-1.09107	1.2424	2.979	9.714	0.566	1.50
	7	-1.07761	1.0593	3.164	11.02	0.556	1.77
	8	-1.06517	0.8901	3.365	12.52	0.546	2.10
	9	-1.05374	0.7347	3.585	14.24	0.538	2.49
	10	-1.04334	0.5931	3.828	16.27	0.530	2.96
	11	-1.03396	0.4656	4.108	18.73	0.523	3.55
	12	-1.02563	0.3523	4.421	21.68	0.518	4.28
	13	-1.01838	0.2537	4.797	25.46	0.513	5.23
	14	-1.01224	0.1702	5.26	30.5	0.51	6.52
	15	-1.00688	0.0973	5.92	38.4	0.51	8.57
	16	-1.00323	0.0476	6.81	50.2	0.51	11.6
	17	-1.00088	0.0157	8.29	73.3	0.50	17.6
	18	-0.99986	0.0018	12.0	152.	0.50	37.6

TABLE XIII
ADIABATIC (N=1) RESULTS FOR pep, L=2

L	ν	E	B	$\langle r_n \rangle$	$\langle r_n^2 \rangle$	γ	$Q_{0, \text{adia}}^{\nu, 2}$
		(W_e)	(eV.)	(a_e)	(a_e^2)	($\pi^{-1} a_{pe}^{-3}$)	(a_e^2)
2	0	-1.19301	2.6290	2.071	4.345	0.649	0.523
	1	-1.17312	2.3585	2.207	5.035	0.632	0.633
	2	-1.15439	2.1036	2.348	5.794	0.616	0.761
	3	-1.13677	1.8640	2.495	6.630	0.602	0.908
	4	-1.12020	1.6386	2.640	7.509	0.589	1.07
	5	-1.10475	1.4229	2.813	8.599	0.576	1.28
	6	-1.09032	1.2323	2.987	9.761	0.565	1.51
	7	-1.07691	1.0499	3.173	11.08	0.555	1.79
	8	-1.06452	0.8813	3.374	12.58	0.546	2.11
	9	-1.05314	0.7265	3.595	14.32	0.537	2.50
	10	-1.04278	0.5856	3.840	16.36	0.530	2.98
	11	-1.03346	0.4588	4.121	18.84	0.522	3.58
	12	-1.02518	0.3462	4.436	21.83	0.517	4.31
	13	-1.01798	0.2483	4.816	25.65	0.512	5.28
	14	-1.01190	0.1656	5.28	30.7	0.51	6.59
	15	-1.00661	0.0936	5.95	38.8	0.51	8.69
	16	-1.00302	0.0448	6.86	51.0	0.51	11.8
	17	-1.00075	0.0139	8.41	75.4	0.50	18.1
	18	-0.99981	0.0012	12.5	164.	0.50	40.6

It is noted that for $N = 1$ (the adiabatic approximation) the present study was not limited to $L = 0$ or $L = 1$. Because the coupling term $g_{1s\sigma_g, 1s\sigma_g}^{(1)}(r_n)$ is the same for any equal-mass, gerade configuration having $L = \text{even}$ and $\Pi_I = +$ or $L = \text{odd}$ and $\Pi_I = -$, the effect of higher orbital angular momentum quantum numbers L is accounted for by the centrifugal (repulsion) term $L(L + 1)/r_n^2$.

The results in Table XI, page 176, for the energy E are compared to those of Cohen, Hiskes, and Riddell (1960) and of Wind (1965) in Table XIV, page 180, for all $L = 0$ vibrational quantum numbers v . From Table XIV, it is seen that the present work has obtained energies more bound than those of Cohen, Hiskes, and Riddell (1960) by $0(10^{-4} W_\mu)$ for energy levels $0 \leq v \leq 14$. For these same energy levels, the present results are $0(10^{-4} W_e)$ more bound than those of Wind (1965). The present results are less tightly bound than those of Cohen, Hiskes, and Riddell (1960) for the uppermost levels, $15 \leq v \leq 18$, by $0(10^{-3} W_e)$. These uppermost levels are more tightly bound than those of Wind (1965) by $0(10^{-4} W_e)$. The present work yielded 19 vibrational levels, in agreement with Cohen, Hiskes, and Riddell (1960), instead of the 20 levels found by Wind (1965). It is worthy of note that the energy levels of Cohen, Hiskes, and Riddell (1960) are more bound than those of Wind (1965) for all but the uppermost levels.

It is concluded that the present study, because of the use of the exact electronic wave function $1s\sigma_g$ and the exact electronic energy, has yielded the best available values of the lower vibrational energy levels

TABLE XIV
COMPARISON OF pep ADIABATIC ($N=1$) ENERGY EIGENVALUES TO RESULTS OF
OTHER AUTHORS FOR $L=0$

ν	E (W_e)	E_{CHR}^a (W_e)	E_{Wind}^b (W_e)	$E_{\text{CHR}}-E$ (W_e)	$E_{\text{Wind}}-E$ (W_e)
0	-1.19460	-1.19450	-1.19428	0.00010	0.00032
1	-1.17463	-1.17453	-1.17431	0.00010	0.00032
2	-1.15581	-1.15573	-1.15550	0.00008	0.00031
3	-1.13812	-1.13804	-1.13781	0.00008	0.00031
4	-1.12147	-1.12144	-1.12121	0.00003	0.00026
5	-1.10595	-1.10590	-1.10567	0.00005	0.00028
6	-1.09144	-1.09140	-1.09117	0.00004	0.00027
7	-1.07796	-1.07793	-1.07770	0.00003	0.00026
8	-1.06550	-1.06547	-1.06525	0.00003	0.00025
9	-1.05404	-1.05401	-1.05381	0.00003	0.00023
10	-1.04361	-1.04358	-1.04338	0.00003	0.00023
11	-1.03421	-1.03416	-1.03399	0.00005	0.00022
12	-1.02586	-1.02580	-1.02564	0.00006	0.00022
13	-1.01858	-1.01851	-1.01836	0.00007	0.00022
14	-1.01241	-1.01234	-1.01219	0.00007	0.00022
15	-1.00702	-1.00735	-1.00718	-0.00033	-0.00016
16	-1.00333	-1.00361	-1.00338	-0.00028	-0.00005
17	-1.00095	-1.00120	-1.00087	-0.00025	0.00008
18	-0.99989	-1.00013	-0.99967	-0.00024	0.00022
19			-0.99946		

^aCohen, Hiskes, and Riddell (1960)

^bWind (1965)

for the system pep. These levels differ only slightly from those of Cohen, Hiskes, and Riddell (1960) and differ to a larger degree from those of Wind (1965). The error in these energy levels is of an order that relativistic corrections and spin interactions can be meaningfully considered.

IV. APPLICATION OF CALCULATED OVERLAP γ_0 TO THE WEAK INTERACTION

The most immediate application of the preceding results is use of the calculated ortho state ($L=1$) overlap, $\gamma_0=0.562$, of the pup system in the formalism of Primakoff (1959) for muon capture in hydrogen, $\mu+p \rightarrow n+\nu$, to obtain an estimate of the weak interaction coupling constants. Primakoff writes

$$\lambda = 2\gamma_0 \cdot \lambda_H \cdot \left[1 + \langle \vec{\sigma} \cdot \vec{\sigma}_1 \rangle \frac{b(u)}{a(u)} \right] \text{ sec}^{-1}, \quad (4.1)$$

where λ_H is the averaged result for the hydrogen atom with a proton as the nucleus and $\langle \vec{\sigma} \cdot \vec{\sigma}_1 \rangle = -2$ for the ortho state ($L=1$) of pup. Further,

$$\lambda_H = n^2 \cdot \left[\left(\frac{m_\mu}{m_e} \right)^5 \frac{\pi \ln 2}{(137)^3 (f\tau_{1/2})_n} \right] \cdot \frac{a(u)}{(g_V^{(\beta)})^2 + 3(g_A^{(\beta)})^2};$$

in which

$$n^2 = \left(\frac{v}{m_\mu} \right)^2 / \left\{ \left(1 + \frac{v}{\sqrt{v^2 + m_p^2}} \right) \cdot \left(1 + \frac{m_\mu}{m_p} \right)^3 \right\},$$

where v is the unique neutrino three-momentum in energy units,

$$v = \frac{\ell^2 - m_n^2}{2\ell},$$

$$Q = m_\mu + m_p - |W_{p\mu}|$$

the masses m_μ , m_e , and m_p of the muon, electron, and proton, respectively, are in energy units, $(f\tau_{1/2})_n$ is the $f\tau_{1/2}$ value of the neutron in β -decay, $g_V^{(\beta)}$ and $g_A^{(\beta)}$ are the vector and axial vector coupling constants in β -decay, using Primakoff's convention,

$$a^{(\mu)} = (G_V^{(\mu)})^2 + 3(\Gamma_A^{(\mu)})^2 ,$$

$$b^{(\mu)} = 2 [G_V^{(\mu)} \cdot (G_A^{(\mu)} - (1/3)G_p^{(\mu)}) - G_A^{(\mu)} \cdot (G_A^{(\mu)} + (2/3)G_p^{(\mu)})] ,$$

$$(\Gamma_A^{(\mu)})^2 = (G_A^{(\mu)})^2 + (1/3)G_p^{(\mu)} \cdot (G_p^{(\mu)} - 2G_A^{(\mu)}) ,$$

$$G_V^{(\mu)} = g_V^{(\mu)} \cdot \left(1 + \frac{\nu}{2m_p}\right) ,$$

$$G_A^{(\mu)} = g_A^{(\mu)} - g_V^{(\mu)} \cdot (1 + \mu_p - \mu_n) \cdot \frac{\nu}{2m_p} ,$$

$$G_p^{(\mu)} = [g_p^{(\mu)} - g_A^{(\mu)} - g_V^{(\mu)} \cdot (1 + \mu_p - \mu_n)] \cdot \frac{\nu}{2m_p} ,$$

and $\mu_p = 1.793$ and $\mu_n = -1.913$ are the anomalous magnetic moments of the proton and neutron, respectively, in units of nuclear magnetons $\frac{e}{2m_p}$, $\hbar = c = 1$.

Using $(f\tau_{1/2})_n = 1213.4$ and $|g_A^{(\beta)}/g_V^{(\beta)}| = 1.18$,

as given by Bhalla (1966), and the masses

$$m_e = 0.511006 \text{ MeV.}, \quad m_\mu = 105.659 \text{ MeV.}, \quad m_p = 938.256 \text{ MeV.}, \text{ and}$$

$$m_n = 939.550 \text{ MeV.}, \quad \text{one obtains}$$

$$\frac{\nu}{m_\mu} = 0.93835,$$

$$\eta^2 = 0.57850,$$

and

$$\lambda = 2\gamma_0 \cdot (29.473) \cdot \frac{a^{(\mu)}}{(g_V^{(\beta)})^2} \cdot \left(1 - 2 \frac{b^{(\mu)}}{a^{(\mu)}}\right) \text{ sec.}^{-1} \quad (4.2)$$

Primakoff (1959) estimates $g_V^{(\mu)} = 0.972 g_V^{(\beta)}$. Letting $f_1 = \frac{v}{2m_p}$,

$f_2 = 1 + \frac{v}{2m_p}$, $f_3 = (1 + \mu_p - \mu_n) \frac{v}{2m_p}$, $c_1 = g_V^{(\mu)} / g_V^{(\beta)}$, $x = g_A^{(\mu)} / g_V^{(\mu)}$, and

$y = g_p^{(\mu)} / g_A^{(\mu)}$, one obtains

$$A \equiv \frac{a^{(\mu)}}{(g_V^{(\beta)})^2} = G_V^2 + 3 \Gamma_A^2$$

and

$$B \equiv \frac{b^{(\mu)}}{(g_V^{(\beta)})^2} = 2 \cdot \left\{ G_V \cdot G_A - \frac{G_p}{3} - G_A \cdot G_A - \frac{2G_p}{3} \right\},$$

where

$$G_V = c_1 \cdot f_2,$$

$$G_A = x - c_1 \cdot f_3,$$

$$G_p = x \cdot (y-1) \cdot f_1 - c_1 \cdot f_3,$$

and

$$\Gamma_A^2 = G_A^2 + \frac{G_p}{3} \cdot (G_p - 2G_A).$$

Then

$$\lambda = 2\gamma_0 \cdot (29.473) \cdot A \cdot \left(1 - 2 \frac{B}{A}\right) \text{ sec}^{-1}, \quad (4.3)$$

where γ_0 is measured in units of the atomic overlap $1/(\pi a_{pu}^3)$, see Equation (3.83).

The capture rate of muons in liquid hydrogen has been measured by Rothberg (1963), Rothberg et al. (1963), Hildebrand (1963), and Rubbia (1964). The measurement $\lambda = 454 \pm 42 \text{ sec.}^{-1}$ by Rothberg et al. (1963) is

the most direct and quotes the smallest error bars. Rothberg et al. (1963) used the best value then available for the overlap, $2\gamma_0 = 1.165$ (Weinberg, 1960), to determine the locus of the values of $g_p^{(\mu)}/g_A^{(\mu)}$ and $g_A^{(\mu)}/g_V^{(\beta)}$ from Equation (4.1) which were consistent with his experimental measurement. Figure 29, page 185, presents similarly the locus determined from Equation (4.3) by the central measurement by Rothberg et al. (1963),

$$\lambda = 464 \text{ sec}^{-1}, \text{ using}$$

$$2\gamma_0 = 1.165 \text{ (Weinberg, 1960),}$$

$$\gamma_0 = 0.500 \text{ (Wessel and Phillipson, 1964), and}$$

$$\gamma_0 = 0.562 \text{ (present work).}$$

The present work is seen to lie between the other two.

Figure 30, page 186, presents the locus of $g_p^{(\mu)}/g_A^{(\mu)}$ versus $g_A^{(\mu)}/g_V^{(\beta)}$ for three muon capture reactions: capture in the ortho state of pnp, capture in He^3 for the channel $\mu + \text{He}^3 \rightarrow \text{H}_1^3 + \nu$, and radiative capture in Ca^{40} . The experimental uncertainty for ortho pnp and He^3 is indicated by loci corresponding to upper and lower error bars on the experimental measurement, augmented, as follows, by uncertainty in the ratio $g_A^{(\beta)}/g_V^{(\beta)}$. Lee and Wu (1965) quote $g_A^{(\beta)}/g_V^{(\beta)} = -1.18 \pm 0.02$, and Rothberg et al. (1963) found $\lambda = (464 \pm 42) \text{ sec}^{-1}$ for pnp. The root mean square of the fractional errors in the capture rate and $g_A^{(\beta)}/g_V^{(\beta)}$ were multiplied by the central measurement of the capture rate to determine the adjusted error bars. Thus, for pnp the error bars were taken

to be $\pm 464 \sqrt{\left(\frac{42}{464}\right)^2 + \left(\frac{0.02}{1.18}\right)^2} \text{ sec}^{-1} = \pm 43 \text{ sec}^{-1}$, and curves were drawn for

FIGURE 29

WEAK INTERACTION COUPLING CONSTANTS FROM CAPTURE IN
ORTHO $p\mu p$ WITH $\lambda = 464/\text{SEC}$.

FIGURE 30

WEAK INTERACTION COUPLING CONSTANTS FROM MUON
CAPTURE IN $p\mu p$, He^3 , AND Ca^{40}

$\lambda = (464 \pm 43) \text{ sec.}^{-1}$. Auerbach et al., (1965) quote the capture rate $\Lambda_{\text{He}^3} = (1505 \pm 46) \text{ sec.}^{-1}$ for He^3 . Adjustment of these error bars for uncertainty in $g_A^{(\beta)}/g_V^{(\beta)}$ led to new error bars $\pm 1505 \sqrt{\left(\frac{46}{1505}\right)^2 + \left(\frac{0.02}{1.18}\right)^2} \text{ sec.}^{-1} = \pm 53 \text{ sec.}^{-1}$, and curves were drawn for $\Lambda_{\text{He}^3} = (1505 \pm 53) \text{ sec.}^{-1}$.

The curves in Figure 30, page 186, drawn for muon capture in ortho pup were obtained from the formulation of Primakoff (1959), described above, using the overlap $\gamma_0 = 0.562$ determined in the present work for ortho ($L=1$) pup. The curves in Figure 30 for muon capture in He^3 were obtained from the formulation of Bietti (1965), using the Irving wave function with exponent $n=0$ and the definitions of

$$\frac{g_p^{(\mu)}}{g_A^{(\mu)}} \equiv \frac{g_p \cdot F_p(q^2)}{g_A \cdot F_A(q^2)} \quad \text{and} \quad \frac{g_A^{(\mu)}}{g_V^{(\beta)}} \equiv \frac{g_A \cdot F_A(q^2)}{g_V \cdot (0.5)} \quad \text{to include}$$

the form factors $F_p(q^2)$ and $F_A(q^2)$. The curves in Figure 30 for radiative capture in Ca^{40} were obtained by using the result obtained by Fearing (1966), $g_p^{(\mu)}/g_A^{(\beta)} = 16.5 \pm 3.1$ at $g_A^{(\mu)}/g_V^{(\beta)} = -1.18$, and drawing lines parallel to those determined by Conversi et al. (1964) for this capture process.

Figure 30, page 186, reveals that the overlap $\gamma_0 = 0.562$ obtained in the present work corresponds to a value of $g_p^{(\mu)}/g_A^{(\mu)} = 13.2 \pm 3.5$ at the currently accepted value of $g_A^{(\mu)}/g_V^{(\beta)} = -1.18$. At $g_A^{(\mu)}/g_V^{(\beta)} = -1.18$ the values allowed by the analysis by Fearing (1966) of the measurement Conversi et al. (1964) for He^3 and by the present work for ortho pup, using the measurement by Rothberg et al. (1963), are $g_p^{(\mu)}/g_A^{(\mu)} = 15.1 \pm 1.5$. Most of

this range also lies within the values allowed by the Ca^{40} analysis done by Conversi et al. (1964).

Figure 30, page 186, also shows that the Bietti (1966) treatment of He^3 capture tends to yield much lower values of $g_p^{(\mu)}/g_A^{(\mu)}$ at $g_A^{(\mu)}/g_V^{(\beta)} = -1.18$, the limits being $g_p^{(\mu)}/g_A^{(\mu)} = 7.5 \begin{cases} +2.4 \\ -1.9 \end{cases}$. These values are not included by either Fearing (1966) or Conversi et al. (1964) and coincide with the present work only for $g_p^{(\mu)}/g_A^{(\mu)} = 9.8 \pm 0.1$ at $g_A^{(\mu)}/g_V^{(\beta)} = -1.18$. The He^3 result at $g_A^{(\mu)}/g_V^{(\beta)} = -1.18$ does, however, lie mostly within the interval that one obtains for $\text{p}\mu\text{p}$ with $\gamma_0 = 0.500$ (Wessel and Phillipson, 1964) and the measurement by Rothberg et al. (1963); but this region is excluded by the result of Fearing (1966) for radiative capture in Ca^{40} .

The intersection of the loci determined in Figure 30, page 186, by the central measurement for muon capture in ortho $\text{p}\mu\text{p}$, He^3 , and Ca^{40} occurs near $g_p^{(\mu)}/g_A^{(\mu)} = 16.2$ and $g_A^{(\mu)}/g_V^{(\beta)} = -1.26$. The region allowed by considering the error bars on these measurements is included by $g_p^{(\mu)}/g_A^{(\mu)} = 16.2 \pm 3.2$ and $g_A^{(\mu)}/g_V^{(\beta)} = -1.26 \begin{cases} +0.05 \\ -0.04 \end{cases}$, corresponding to the cross-hatched area of Figure 30.

This region, $-1.30 \leq g_A^{(\mu)}/g_V^{(\beta)} \leq -1.21$, includes the region $g_A^{(\beta)}/g_V^{(\beta)} = -(1.25 \pm 0.03)$, quoted by Lee and Wu (1965), that is obtained from the asymmetry of neutrinos from beta decay of neutrons. However, the region $-1.30 \leq g_A^{(\mu)}/g_V^{(\beta)} \leq -1.21$ does not include the region $-1.20 \leq g_A^{(\beta)}/g_V^{(\beta)} \leq -1.16$ currently preferred by Lee and Wu (1965) for beta decay. Lee and Wu (1965) further quote $0.97 < g_A^{(\mu)}/g_A^{(\beta)} < 1$, as

determined by high energy neutrino experiments, which would tend to lower the preferred values of $|g_A^{(\mu)}/g_V^{(\beta)}|$.

The He^3 capture locus is chiefly responsible for the large values of $|g_A^{(\mu)}/g_V^{(\beta)}|$ determined from the intersection of the three regions determined by muon capture in ortho $\text{p}\mu\text{p}$, He^3 , and Ca^{40} . The wave function used in the He^3 calculation of the nuclear matrix element is assumed to be a nuclear s -state, suggesting that the effect of higher terms on the calculated capture rate should be studied, along with the corresponding shift of the locus of the He^3 capture experiment in the plane of $g_p^{(\mu)}/g_A^{(\mu)}$ and $g_A^{(\mu)}/g_V^{(\beta)}$. The slope of the He^3 locus in Figure 30, page 186, is very nearly perpendicular to that of Ca^{40} , as determined by Conversi et al., (1964), and the slope of the ortho $\text{p}\mu\text{p}$ capture locus is also different from that of either He^3 or Ca^{40} . Thus, further study of these three types of muon capture, both theoretically and experimentally, offers the possibility of reducing the uncertainty in the quantitative values of those weak interaction coupling constants allowed by the theory of the universal Fermi interaction.

The present work may be viewed as having set a new upper bound on the value of $g_p^{(\mu)}/g_A^{(\mu)}$ at a given value of $g_A^{(\mu)}/g_V^{(\beta)}$.

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APPENDIXES

APPENDIX A

GEOMETRY

The coordinate systems used in the present work are presented in Figure 1, page 13. Cartesian coordinates fixed in the laboratory at the center of mass of the two nuclei are represented by (X_L, Y_L, Z_L) . Body-fixed Cartesian coordinates, attached to the two nuclei, are represented by (x_n, y_n, z_n) , with the z_n -axis along the internuclear axis $\vec{r}_n$ and the origin at the center of mass of the two nuclei. The Euler angles, in the order in which they are applied to the nuclear coordinate system, are ϕ_n about the z_L -axis, θ_n about the y_n -axis, and ϕ about the z_n -axis. The Euler angles θ_n and ϕ_n serve to specify the orientation of the internuclear axis $\vec{r}_n$, which is taken as the z_n -axis. The third Euler angle specifies the azimuth of the muon in the nuclear coordinate system (x_n, y_n, z_n) . Note that $\hat{e}_{x_n} = \hat{e}_{\theta_n}$, $\hat{e}_{y_n} = \hat{e}_{\phi_n}$, and $\hat{e}_{z_n} = \hat{e}_{r_n}$.

Figure 31, page 197, shows an isometric view of the muon coordinates in the nuclear system (x_n, y_n, z_n) . Figure 32, page 198, represents a view perpendicular to the plane of the two nuclei and the muon. The vectors $\vec{r}_{\mu 1}$, $\vec{r}_{\mu 2}$, $\vec{r}_n$, and $\vec{R}_\mu$ show in true length in Figure 32, as does the polar angle θ of the muon relative to the $\vec{r}_n$ axis.

One seeks to calculate the three gradients, $\vec{\nabla}_n(\xi)$, $\vec{\nabla}_n(\eta)$, and $\vec{\nabla}_n(\phi)$, which characterize the effect of the nuclear motion on the coordinates of the muon relative to the nuclear frame. The laboratory coordinates of the

FIGURE 31

MOON COORDINATES IN THE BODY-FIXED COORDINATE SYSTEM

FIGURE 32

PLANE CONTAINING THE TWO NUCLEI AND THE MUON

muon in the frame (x_L, y_L, z_L) are understood to be fixed during the process of differentiation with respect to the nuclear coordinates (r_n, θ_n, ϕ_n) .

The gradients are used to calculate the coupling between the nuclear motion and that of the muon.

Using the definition of the prolate spheroidal coordinates as given in Equation (2.26), $\xi = \frac{r_{\mu 1} + r_{\mu 2}}{r_n}$, $\eta = \frac{r_{\mu 1} - r_{\mu 2}}{r_n}$, and the Euler angle ϕ (cf. Lowan, 1965), one has

$$\vec{\nabla}_n(r_n \xi) = \vec{\nabla}_n(r_{\mu 1}) + \vec{\nabla}_n(r_{\mu 2}).$$

Also,

$$\vec{\nabla}_n(r_n \xi) = r_n \vec{\nabla}_n(\xi) + \xi \hat{e}_{r_n},$$

since $\vec{\nabla}_n(r_n) = \hat{e}_{r_n}$. From these, one obtains

$$\vec{\nabla}_n(\xi) = \frac{1}{r_n} \{ \vec{\nabla}_n(r_{\mu 1}) + \vec{\nabla}_n(r_{\mu 2}) - \xi \hat{e}_{r_n} \}. \quad (\text{A.1})$$

Recall that

$$f_1 = \frac{m_1}{m_1 + m_2}, \quad f_2 = \frac{m_2}{m_1 + m_2}, \quad \text{and } f_1 + f_2 = 1. \quad (2.2)$$

From Figure 32, page 198, $\vec{r}_{\mu 1} = \vec{R}_\mu - f_2 \vec{r}_n$; thus, one has

$$\vec{\nabla}_n(r_{\mu 1}) = \frac{(\vec{R}_\mu - f_2 \vec{r}_n)}{|\vec{R}_\mu - f_2 \vec{r}_n|} \cdot (-f_2) = -f_2 \hat{e}_{r_{\mu 1}}. \quad (\text{A.2})$$

Similarly, $\vec{r}_{\mu 2} = \vec{R}_\mu + f_1 \vec{r}_n$, and

$$\vec{\nabla}_n(r_{\mu 2}) = \frac{(\vec{R}_\mu + f_1 \vec{r}_n)}{|\vec{R}_\mu + f_1 \vec{r}_n|} \cdot (f_1) = f_1 \hat{e}_{r_{\mu 2}}. \quad (\text{A.3})$$

Therefore,

$$\vec{v}_n(\xi) = \frac{1}{r_n} (-f_2 \hat{e}_{r_{\mu 1}} + f_1 \hat{e}_{n_{\mu 2}} - \xi \hat{e}_{r_n}). \quad (\text{A.4})$$

From Figure 31, page 197, one obtains

$$\vec{r}_{\mu 1} = -r_{\mu 1} \cos A \hat{e}_{r_n} + r_{\mu 1} \sin A \hat{e}_v, \quad (\text{A.5})$$

where $\hat{e}_v = \cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}$. (A.6)

Thus, $\hat{e}_{r_{\mu 1}} = -\cos A \hat{e}_{r_n} + \sin A \hat{e}_v$. (A.7)

From the law of cosines one has

$$\cos A = \frac{r_n^2 + r_{\mu 1}^2 - r_{\mu 2}^2}{2r_n r_{\mu 1}} \quad (\text{A.8})$$

One notes that

$$r_{\mu 1} = \frac{r_n}{2} (\xi + \eta) \text{ and } r_{\mu 2} = \frac{r_n}{2} (\xi - \eta), \quad (\text{A.9})$$

so that

$$\cos A = \frac{1 + \xi \eta}{\xi + \eta} \text{ and } \sin A = \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{\xi + \eta}. \quad (\text{A.10})$$

Thus,

$$\hat{e}_{r_{\mu 1}} = -\left(\frac{1 + \xi \eta}{\xi + \eta}\right) \hat{e}_{r_n} + \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{\xi + \eta} (\cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}). \quad (\text{A.11})$$

From Figure 32, page 198, one obtains

$$h = r_{\mu 1} \cos A = \frac{r_n}{2} (1 + \xi \eta), \quad (\text{A.12})$$

$$v = r_{\mu 1} \sin A = \frac{r_n}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)}, \quad (\text{A.13})$$

$$z = f_2 r_n - h = -\frac{r_n}{2} [\xi\eta + (f_1 - f_2)], \quad (\text{A.14})$$

$$R_\mu = \sqrt{z^2 + v^2} = \frac{r_n}{2} [\xi^2 + \eta^2 - 1 + 2(f_1 - f_2)\xi\eta + (f_1 - f_2)^2]^{1/2}, \quad (\text{A.15})$$

and

$$\vec{r}_{\mu 2} = (r_n - h) \hat{e}_{r_n} + \vec{v}. \quad (\text{A.16})$$

Thus,

$$\begin{aligned} \hat{e}_{r_{\mu 2}} &= \frac{\left[r_n - \frac{r_n}{2} (1 + \xi\eta) \right] \hat{e}_{r_n} + \frac{r_n}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \hat{e}_v}{\frac{r_n}{2} (\xi - \eta)} \\ &= \frac{1}{(\xi - \eta)} \cdot \left\{ (1 - \xi\eta) \hat{e}_{r_n} + \sqrt{(\xi^2 - 1)(1 - \eta^2)} (\cos\phi \hat{e}_{\theta_n} + \sin\phi \hat{e}_{\phi_n}) \right\}. \end{aligned} \quad (\text{A.17})$$

From the above, one obtains

$$\begin{aligned} \vec{\nabla}_n(\xi) &= \frac{1}{r_n} \left\{ \left[(-f_2) \left(-\frac{1 + \xi\eta}{\xi + \eta} \right) + (f_1) \left(\frac{1 - \xi\eta}{\xi - \eta} \right) - \xi \right] \hat{e}_{r_n} \right. \\ &\quad \left. + \left(\frac{-f_2}{\xi + \eta} + \frac{f_1}{\xi - \eta} \right) \sqrt{(\xi^2 - 1)(1 - \eta^2)} \hat{e}_v \right\} \\ &= \frac{1}{r_n(\xi^2 - \eta^2)} \left\{ -\xi(\xi^2 - 1) \hat{e}_{r_n} + \eta \sqrt{(\xi^2 - 1)(1 - \eta^2)} \hat{e}_v \right. \\ &\quad \left. + (f_1 - f_2) \left[-\eta(\xi^2 - 1) \hat{e}_{r_n} + \xi \sqrt{(\xi^2 - 1)(1 - \eta^2)} \hat{e}_v \right] \right\}, \end{aligned} \quad (\text{A.18})$$

where $(f_1 - f_2) = 0$ for the equal-mass (homonuclear) case.

Proceeding in a like manner to obtain $\vec{\nabla}_n(\eta)$, one has

$$r_{n\eta} = r_{\mu 1} - r_{\mu 2}$$

and

$$\vec{v}_n(r_n \eta) = r_n \vec{v}_n(\eta) + \eta \hat{e}_{r_n} = \vec{v}_n(r_{\mu 1}) - \vec{v}_n(r_{\mu 2}).$$

Thus,

$$\begin{aligned} \vec{v}_n(\eta) &= \frac{1}{r_n} (-f_2 \hat{e}_{r_{\mu 1}} - f_1 \hat{e}_{r_{\mu 2}} - \eta \hat{e}_{r_n}) \\ &= \frac{1}{r_n} \left\{ \left[-f_2 \left(-\frac{1+\xi\eta}{\xi+\eta} \right) - f_1 \left(\frac{1-\xi\eta}{\xi-\eta} \right) - \eta \right] \hat{e}_{r_n} \right. \\ &\quad \left. + \left(-\frac{f_2}{\xi+\eta} - \frac{f_1}{\xi-\eta} \right) \sqrt{(\xi^2-1)(1-\eta^2)} \hat{e}_v \right\} \\ &= -\frac{1}{r_n(\xi^2-\eta^2)} \left\{ \eta(1-\eta^2) \hat{e}_{r_n} + \xi \sqrt{(\xi^2-1)(1-\eta^2)} \hat{e}_v \right. \\ &\quad \left. + (f_1-f_2) \left[\xi(1-\eta^2) \hat{e}_{r_n} + \eta \sqrt{(\xi^2-1)(1-\eta^2)} \hat{e}_v \right] \right\}, \quad (\text{A.19}) \end{aligned}$$

where $f_1-f_2 = 0$ for the equal-mass (homonuclear) case.

One now seeks to find

$$\vec{v}_n(\phi) = \frac{1}{r_n} \frac{\partial \phi}{\partial \theta_n} \hat{e}_{\theta_n} + \frac{1}{r_n \sin \theta_n} \frac{\partial \phi}{\partial \phi_n} \hat{e}_{\phi_n}. \quad (\text{A.20})$$

Let the spherical coordinates of the muon in the laboratory system

(x_L, y_L, z_L) be $(r_\mu, \theta_\mu, \phi_\mu)$, where the origin is taken to be at the center of mass of the two nuclei. Let the corresponding Cartesian coordinates of

the muon in the laboratory system (x_L, y_L, z_L) be $\vec{x}_\mu = (x_\mu, y_\mu, z_\mu)$,

such that the vector $\vec{R}_\mu$ has components

$$x_\mu \hat{e}_{x_L} = R_\mu \sin \theta_\mu \cos \phi_\mu \hat{e}_{x_L},$$

$$y_\mu \hat{e}_{y_L} = R_\mu \sin \theta_\mu \sin \phi_\mu \hat{e}_{y_L},$$

and

$$z_{\mu} \hat{e}_{z_L} = R_{\mu} \cos \theta_{\mu} \hat{e}_{z_L}$$

Similarly, let the spherical coordinates of the muon in the nuclear system (x_n, y_n, z_n) be (R_{μ}, θ, ϕ) with the corresponding Cartesian coordinates $\vec{x} = (x, y, z)$:

$$x \hat{e}_{x_n} = R_{\mu} \sin \theta \cos \phi \hat{e}_{x_n},$$

$$y \hat{e}_{y_n} = R_{\mu} \sin \theta \sin \phi \hat{e}_{y_n},$$

and

$$z \hat{e}_{z_n} = R_{\mu} \cos \theta \hat{e}_{z_n}.$$

Note that $\hat{e}_{x_n} = \hat{e}_{\theta_n}$, $\hat{e}_{y_n} = \hat{e}_{\phi_n}$, and $\hat{e}_{z_n} = \hat{e}_{r_n}$.

Rotation of a Cartesian coordinate system about its z-axis by the angle α may be accomplished by

$$\vec{V}_2 = \bar{R}_z(\alpha) \vec{V}_1,$$

where $\vec{V}_2 = (x_2, y_2, z_2)$ are the Cartesian coordinates of a vector after rotation of the coordinate system, $\vec{V}_1 = (x_1, y_1, z_1)$ are the Cartesian coordinates of a vector before rotation of the coordinate system, α is positive for counter clockwise rotations, and

$$\bar{R}_z(\alpha) = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Similarly, rotation of a coordinate system about its y-axis by the angle β yields

$$\vec{V}_2 = \bar{R}_y(\beta) \vec{V}_1,$$

where

$$\bar{R}_y(\beta) = \begin{pmatrix} \cos \beta & 0 & -\sin \beta \\ 0 & 1 & 0 \\ \sin \beta & 0 & \cos \beta \end{pmatrix}$$

The transformation of muon coordinates $\vec{x}_\mu$ from the laboratory system to $\vec{x}$ in the nuclear system is given by

$$\vec{x} = \bar{R}_{y_n}(\theta_n) \bar{R}_{z_L}(\phi_n) \vec{x}_\mu,$$

where ϕ_n is the first Euler angle, θ_n is the second Euler angle,

$$\vec{x}_\mu = \begin{pmatrix} R_\mu \sin \theta_\mu \cos \phi_\mu \\ R_\mu \sin \theta_\mu \sin \phi_\mu \\ R_\mu \cos \theta_\mu \end{pmatrix},$$

$$\bar{R}_{z_L}(\phi_n) = \begin{pmatrix} \cos \phi_n & \sin \phi_n & 0 \\ -\sin \phi_n & \cos \phi_n & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\bar{R}_{y_n}(\theta_n) = \begin{pmatrix} \cos \theta_n & 0 & -\sin \theta_n \\ 0 & 1 & 0 \\ \sin \theta_n & 0 & \cos \theta_n \end{pmatrix},$$

and

$$\vec{x} = \begin{pmatrix} R_\mu \sin \theta \cos \phi \\ R_\mu \sin \theta \sin \phi \\ R_\mu \cos \theta \end{pmatrix}.$$

The magnitude R_μ may be cancelled from both sides of the equation, and one obtains

$$\begin{pmatrix} \sin \theta & \cos \phi \\ \sin \theta & \sin \phi \\ \cos \theta \end{pmatrix} = \begin{pmatrix} \cos \theta_n \cos \phi_n & \cos \theta_n \sin \phi_n & -\sin \theta_n \\ -\sin \theta_n \cos \phi_n & \cos \theta_n \sin \phi_n & 0 \\ \sin \theta_n \cos \phi_n & \sin \theta_n \sin \phi_n & \cos \theta_n \end{pmatrix} \begin{pmatrix} \sin \theta_\mu \cos \phi_\mu \\ \sin \theta_\mu \sin \phi_\mu \\ \cos \theta_\mu \end{pmatrix}$$

These three equations may be expressed as

$$\sin \theta \cos \phi = \cos \theta_n \sin \theta_\mu \cos (\phi_\mu - \phi_n) - \sin \theta_n \cos \theta_\mu, \quad (\text{A.21})$$

$$\sin \theta \sin \phi = \sin \theta_\mu \cos (\phi_\mu - \phi_n), \quad (\text{A.22})$$

and

$$\cos \theta = \sin \theta_n \sin \theta_\mu \cos (\phi_\mu - \phi_n) + \cos \theta_n \cos \theta_\mu. \quad (\text{A.23})$$

Recall that the laboratory coordinates R_μ, θ_μ , and ϕ_μ of the muon are to held constant during differentiation with respect to the nuclear coordinates r_n, θ_n , and ϕ_n . One seeks to obtain $\frac{\partial \phi}{\partial \theta_n}$ and $\frac{\partial \phi}{\partial \phi_n}$ and to eliminate the laboratory coordinates. Differentiation with respect to θ_n of Equation (A.21) and (A.22) yields, respectively,

$$\begin{aligned} \cos \theta \frac{\partial \theta}{\partial \theta_n} \cos \phi - \sin \theta \sin \phi \frac{\partial \phi}{\partial \theta_n} &= -\sin \theta_n \sin \theta_\mu \\ &\cdot \cos (\phi_\mu - \phi_n) - \cos \theta_n \cos \theta_\mu \end{aligned} \quad (\text{A.24})$$

and

$$\cos \theta \frac{\partial \theta}{\partial \theta_n} \sin \phi + \sin \theta \cos \phi \frac{\partial \phi}{\partial \theta_n} = 0. \quad (\text{A.25})$$

From Equation (A.25)

$$\cos \theta \frac{\partial \theta}{\partial \theta_n} = -\sin \theta \cot \phi \frac{\partial \phi}{\partial \theta_n}, \quad (\text{A.26})$$

and from Equation (A.23)

$$\sin \theta_n \sin \theta_\mu \cos (\phi_\mu - \phi_n) = \cos \theta - \cos \theta_n \cos \theta_\mu. \quad (\text{A.27})$$

Substitution of Equations (A.26) and (A.27) in Equation (A.24) yields

$$\frac{\sin \theta}{\sin \phi} (\cos^2 \phi + \sin^2 \phi) \frac{\partial \phi}{\partial \theta_n} = \cos \theta;$$

from which one obtains

$$\frac{\partial \phi}{\partial \theta_n} = \cot \theta \sin \phi \quad . \quad (\text{A.28})$$

Differentiation of Equations (A.21) and (A.23) with respect to ϕ_n yields, respectively,

$$\begin{aligned} \cos \theta \frac{\partial \theta}{\partial \phi_n} \cos \phi - \sin \theta \sin \phi \frac{\partial \phi}{\partial \phi_n} &= \cos \theta_n \sin \theta_\mu \cdot \\ \cdot \sin (\phi_\mu - \phi_n) &= \cos \theta_n \sin \theta \sin \phi \end{aligned} \quad (\text{A.29})$$

and

$$\begin{aligned} -\sin \theta \frac{\partial \theta}{\partial \phi_n} &= \sin \theta_n \sin \theta_\mu \sin (\phi_\mu - \phi_n) \\ &= \sin \theta_n \sin \theta \sin \phi \quad , \end{aligned} \quad (\text{A.30})$$

in which one has used Equation (A.22) to replace $\sin \theta_\mu \sin (\phi_\mu - \phi_n)$.

Solution of Equation (A.30) for $\frac{\partial \theta}{\partial \phi_n}$ and substitution in Equation (A.29) yields

$$\frac{\partial \phi}{\partial \phi_n} = -(\cot \theta \cos \phi \sin \theta_n + \cos \theta_n). \quad (\text{A.31})$$

From Figure 32, page 198, one has

$$\cot \theta = \frac{z}{v} = - \frac{\xi \eta + (f_1 - f_2)}{\sqrt{(\xi^2 - 1)(1 - \eta^2)}} \quad . \quad (\text{A.32})$$

Substitution of Equations (A.28), (A.31), and (A.32) in Equation (A.20) yields

$$\vec{v}_n(\phi) = \left\{ - \frac{\xi \eta + (f_1 - f_2)}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \cdot \sin \phi \right\} \hat{e}_{\theta_n}$$

$$+ \left\{ \frac{\xi \eta + (f_1 - f_2)}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \cdot \cos \phi - \frac{\cot \theta_n}{r_n} \right\} \hat{e}_{\phi_n}, \quad (\text{A.33})$$

where $f_1 - f_2 = 0$ for the equal-mass (homonuclear) case.

One notes that $\vec{V}_n(\phi)$ may be expressed as

$$\vec{V}(\phi) = \frac{\xi \eta + (f_1 - f_2)}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \hat{e}_u - \frac{\cot \theta_n}{r_n} \hat{e}_{\phi_n}, \quad (\text{A.34})$$

where

$$\hat{e}_u = -\sin \phi \hat{e}_{\theta_n} + \cos \phi \hat{e}_{\phi_n}. \quad (\text{A.35})$$

The fact that $\hat{e}_u$ is a unit vector may be checked by the operation

$$\hat{e}_u \cdot \hat{e}_u = \sin^2 \phi + \cos^2 \phi = 1.$$

The unit vector $\hat{e}_u$ lies in the plane of $\hat{e}_{\theta_n}$ and $\hat{e}_{\phi_n}$; thus,

$$\hat{e}_u \cdot \hat{e}_{r_n} = 0. \quad (\text{A.36})$$

The unit vector $\hat{e}_u$ has an azimuth of $\phi + \frac{\pi}{2}$ and is consequently perpendicular to $\hat{e}_v$:

$$\hat{e}_u \cdot \hat{e}_v = -\cos \phi \sin \phi + \cos \phi \sin \phi = 0. \quad (\text{A.37})$$

These results are summarized below for the equal-mass (homonuclear) case:

$$\vec{V}_n(\xi) = \frac{1}{r_n(\xi^2 - \eta^2)} \left\{ -\xi(\xi^2 - 1) \hat{e}_{r_n} + \eta \sqrt{(\xi^2 - 1)(1 - \eta^2)} \right\} \hat{e}_v, \quad (\text{A.38})$$

$$\vec{V}_n(\eta) = -\frac{1}{r_n(\xi^2 - \eta^2)} \left\{ \eta(1 - \eta^2) \hat{e}_{r_n} + \xi \sqrt{(\xi^2 - 1)(1 - \eta^2)} \right\} \hat{e}_v, \quad (\text{A.39})$$

and

$$\vec{v}_n(\phi) = \frac{\xi \eta}{r_n \sqrt{(\xi^2 - 1)(1 - \eta^2)}} \hat{e}_u - \frac{\cot \theta_n}{r_n} \hat{e}_{\phi_n}, \quad (\text{A.40})$$

where

$$\begin{aligned} \hat{e}_v &= \cos \phi \hat{e}_{\theta_n} + \sin \phi \hat{e}_{\phi_n}, \\ \hat{e}_u &= -\sin \phi \hat{e}_{\theta_n} + \cos \phi \hat{e}_{\phi_n}, \\ \hat{e}_{r_n} \cdot \hat{e}_v &= 0, \quad \hat{e}_{r_n} \cdot \hat{e}_u = 0, \text{ and } \hat{e}_v \cdot \hat{e}_u = 0. \end{aligned} \quad (\text{A.41})$$

APPENDIX B

ORTHONORMALITY PROPERTIES OF THE ELECTRONIC WAVE FUNCTIONS

Schrodinger's equation defining the electronic states is given above in the form

$$\left(-\nabla_{\mu}^2 - \frac{2}{r_{\mu 1}} - \frac{2}{r_{\mu 2}} \right) \psi_{iK}(\xi, \eta, \phi; r_n) = W_{iK}(r_n) \psi_{iK}(\xi, \eta, \phi; r_n). \quad (2.25)$$

Note that $r_{\mu 1} = \frac{r_n}{2} \cdot (\xi + \eta)$ and $r_{\mu 2} = \frac{r_n}{2} \cdot (\xi - \eta)$; thus, the electronic potential becomes

$$v = -\frac{2}{r_{\mu 1}} - \frac{2}{r_{\mu 2}} = -2 \cdot \left[\frac{2}{r_n (\xi + \eta)} + \frac{2}{r_n (\xi - \eta)} \right]$$

or

$$v(\xi, \eta; r_n) = -\frac{8\xi}{r_n (\xi^2 - \eta^2)}.$$

Substitution of the electronic potential in Equation (2.25) yields

$$\left(-\nabla_{\mu}^2 - \frac{8\xi}{r_n (\xi^2 - \eta^2)} \right) \psi_{iK} = W_{iK} \psi_{iK}$$

or

$$\nabla_{\mu}^2 \psi_{iK} = - \left(\frac{8\xi}{r_n (\xi^2 - \eta^2)} + W_{iK} \right) \psi_{iK}. \quad (B.1)$$

From the symmetric form of Green's theorem (Irving and Mullineax, 1959) one has

$$\begin{aligned} \int_{R_{\mu}} d^3R_{\mu} \psi_{jK} \nabla_{\mu}^2 \psi_{iK} - \psi_{iK} \nabla_{\mu}^2 \psi_{jK} &= \int_S (\psi_{jK} \vec{\nabla}_{\mu} \psi_{iK} \\ &- \psi_{iK} \vec{\nabla}_{\mu} \cdot \psi_{jK}) \cdot d^2\vec{S}, \end{aligned}$$

where the surface integral on the right vanishes because $\psi_{iK'}(\xi, \eta, \phi; r_n) \xrightarrow{\xi \rightarrow \infty} 0$ and $\psi_{jK}(\xi, \eta, \phi; r_n) \xrightarrow{\xi \rightarrow \infty} 0$.

One has obtained

$$\int_{R_\mu} d^3 R_\mu \psi_{jK} \nabla_\mu^2 \psi_{iK'} = \int_{R_\mu} d^3 R_\mu \psi_{iK'} \nabla_\mu^2 \psi_{jK} .$$

Substitution of Equation (B.1) yields

$$\begin{aligned} & - \int_{R_\mu} d^3 R_\mu \psi_{jK} \left(\frac{8\xi}{r_n(\xi^2 - \eta^2)} + W_{iK'} \right) \psi_{iK'} \\ & = - \int_{R_\mu} d^3 R_\mu \psi_{iK'} \left(\frac{8\xi}{r_n(\xi^2 - \eta^2)} + W_{jK} \right) \psi_{jK} , \end{aligned}$$

or

$$(W_{iK'} - W_{jK}) \int_{R_\mu} d^3 R_\mu \psi_{jK} \psi_{iK'} = 0 . \quad (B.2)$$

Equation (B.2) proves the orthonormality of the electronic wave functions:

$$\int_{R_\mu} d^3 R_\mu \psi_{jK} \psi_{iK'} = 0 , \quad j \neq i, K \neq K' .$$

The normalization of these functions is chosen such that

$$\int_{R_\mu} d^3 R_\mu |\psi_{iK}|^2 = 1 .$$

The orthonormality of the electronic wave functions may be summarized by

$$\int_{R_\mu} d^3 R_\mu \psi_{jK} \psi_{iK'} = \delta_{ji} \delta_{KK'} , \quad (B.3)$$

where the volume element is $d^3 R_\mu = \frac{r_n^3 (\xi^2 - \eta^2)}{8} d\xi d\eta d\phi$ and

$$\psi_{iK'}(\xi, \eta, \phi; r_n) = \mathcal{N}_{iK'}(r_n) \Lambda_{iK'}(\xi, r_n) M_{iK'}(\eta, r_n) \rho_{K'}^{\tau\phi}(\phi) . \quad (2.27)$$

An azimuthal function $\rho_{K-}^{\tau\phi}(\phi)$ obeys the differential equation

$$\frac{d^2 \rho_{K-}^{\tau\phi}}{d\phi^2} + K^{-2} \rho_{K-}^{\tau\phi} = 0. \quad (\text{B.4})$$

Consider a second such function, having quantum number K :

$$\frac{d^2 \rho_K^{\tau\phi}}{d\phi^2} + K^2 \rho_K^{\tau\phi} = 0. \quad (\text{B.5})$$

Multiplication of Equation (B.4) by $\rho_K^{\tau\phi}$ and equation (B.5) by $\rho_{K-}^{\tau\phi}$, subtraction of the two equations, and integration over $d\phi$ yields

$$\begin{aligned} \int_0^{2\pi} \left(\rho_K^{\tau\phi} \frac{d^2 \rho_{K-}^{\tau\phi}}{d\phi^2} - \rho_{K-}^{\tau\phi} \frac{d^2 \rho_K^{\tau\phi}}{d\phi^2} \right) d\phi + (K^{-2} - K^2) \\ \cdot \int_0^{2\pi} \rho_K^{\tau\phi} \rho_{K-}^{\tau\phi} d\phi = 0. \end{aligned} \quad (\text{B.6})$$

Integration by parts yields

$$\begin{aligned} \int_0^{2\pi} \rho_K^{\tau\phi} \frac{d^2 \rho_{K-}^{\tau\phi}}{d\phi^2} d\phi &= \left\{ \rho_K^{\tau\phi} \frac{d \rho_{K-}^{\tau\phi}}{d\phi} - \int \frac{d \rho_K^{\tau\phi}}{d\phi} \frac{d \rho_{K-}^{\tau\phi}}{d\phi} d\phi \right\}_0^{2\pi} \\ &= \left\{ \rho_K^{\tau\phi} \frac{d \rho_{K-}^{\tau\phi}}{d\phi} - \frac{d \rho_K^{\tau\phi}}{d\phi} \rho_{K-}^{\tau\phi} \right\}_{\phi=0}^{2\pi} + \int_0^{2\pi} \rho_{K-}^{\tau\phi} \frac{d^2 \rho_K^{\tau\phi}}{d\phi^2} d\phi. \end{aligned}$$

One notes that $\rho_{K-}^{\tau\phi}$, $\rho_K^{\tau\phi}$, and their derivatives are periodic in ϕ , such that

$$\rho_K^{\tau\phi}(2\pi) = \rho_K^{\tau\phi}(0), \quad \rho_{K-}^{\tau\phi}(2\pi) = \rho_{K-}^{\tau\phi}(0),$$

$$\frac{d \rho_K^{\tau\phi}(2\pi)}{d\phi} = \frac{d \rho_K^{\tau\phi}(0)}{d\phi}, \quad \text{and} \quad \frac{d \rho_{K-}^{\tau\phi}(2\pi)}{d\phi} = \frac{d \rho_{K-}^{\tau\phi}(0)}{d\phi}.$$

The bracket above vanishes, and one has

$$\int_0^{2\pi} \rho_K^{\tau\phi} \frac{d^2 \rho_{K'}^{\tau\phi}}{d\phi^2} d\phi = \int_0^{2\pi} \rho_{K'}^{\tau\phi} \frac{d^2 \rho_K^{\tau\phi}}{d\phi^2} d\phi.$$

Substitution of this result in Equation (B.6) yields

$$(K'^2 - K^2) \int_0^{2\pi} \rho_K^{\tau\phi} \rho_{K'}^{\tau\phi} d\phi = 0$$

or

$$\int_0^{2\pi} \rho_K^{\tau\phi} \rho_{K'}^{\tau\phi} d\phi = 0, \quad K \neq K'.$$

The azimuthal function is chosen to have the normalization

$$\int_0^{2\pi} |\rho_K^{\tau\phi}|^2 d\phi = 2\pi.$$

One may thus write

$$\int_0^{2\pi} \rho_K^{\tau\phi} \rho_{K'}^{\tau\phi} d\phi = 2\pi \delta_{K,K'}. \quad (\text{B.7})$$

Let

$$F_{iK}(\xi, n; r_n) = \mathcal{N}_{iK}(r_n) \Lambda_{iK}(\xi, r_n) M_{iK}(n, r_n), \quad (2.110)$$

such that

$$\psi_{iK}(\xi, n, \phi; r_n) = F_{iK}(\xi, n; r_n) \rho_K^{\tau\phi}(\phi). \quad (\text{B.8})$$

Substitution of Equation (B.8) in Equation (B.3) yields

$$\left\{ \frac{r_n^3}{8} \int_{\xi=1}^{\infty} d\xi \int_{n=-1}^1 dn (\xi^2 - n^2) F_{jK} F_{iK} \right\} \int_0^{2\pi} d\phi \rho_K^{\tau\phi} \rho_{K'}^{\tau\phi} = \delta_{ji}.$$

In turn, substitution of Equation (B.7) in the above yields

$$\frac{\pi r_n^3}{4} \int_{\xi=1}^{\infty} d\xi \int_{\eta=0}^{\infty} d\eta (\xi^2 - \eta^2) F_{jK} F_{iK'} \delta_{K,K'} = \delta_{j,i} \quad (B.9)$$

Note that this result for the functions $F_{iK}(\xi, \eta; r_n)$ and $F_{jK}(\xi, \eta; r_n)$ states that K' must equal K in order that the functions be orthogonal.

An "inner" function $M_{iK}(\eta, r_n)$, having $K' = K$, obeys the differential equation (Bates, Ledsham, and Stewart, 1953)

$$\frac{d}{d\eta} \left\{ (1-\eta^2) \frac{dM_{iK}}{d\eta} \right\} + \left\{ -A_{iK} + p_{iK}^2 \eta^2 - \frac{K^2}{1-\eta^2} \right\} M_{iK} = 0. \quad (B.10)$$

Consider a different "inner" function $M_{jK}(\eta, r_n)$, which has the same value of K :

$$\frac{d}{d\eta} \left\{ (1-\eta^2) \frac{dM_{jK}}{d\eta} \right\} + \left\{ -A_{jK} + p_{jK}^2 \eta^2 - \frac{K^2}{1-\eta^2} \right\} M_{jK} = 0. \quad (B.11)$$

Multiplication of Equation (B.10) by M_{jK} and Equation (B.11) by M_{iK} , subtraction of the two, and integration over $d\eta$ yields

$$\begin{aligned} & \int_{-1}^1 d\eta \left\{ M_{jK} \frac{d}{d\eta} (1-\eta^2) \frac{dM_{iK}}{d\eta} - M_{iK} \frac{d}{d\eta} (1-\eta^2) \frac{dM_{jK}}{d\eta} \right\} \\ &= (A_{iK} - A_{jK}) \int_{-1}^1 d\eta M_{jK} M_{iK} \\ &- (p_{iK}^2 - p_{jK}^2) \int_{-1}^1 d\eta \eta^2 M_{jK} M_{iK}. \end{aligned} \quad (B.12)$$

Integration by parts yields

$$\begin{aligned} \int_{-1}^1 d\eta M_{jK} \frac{d}{d\eta} (1-\eta^2) \frac{dM_{iK}}{d\eta} &= - \int_{-1}^1 d\eta (1-\eta^2) \frac{dM_{jK}}{d\eta} \frac{dM_{iK}}{d\eta} \\ &= \int_{-1}^1 d\eta M_{iK} \frac{d}{d\eta} \left[(1-\eta^2) \frac{dM_{jK}}{d\eta} \right]. \end{aligned} \quad (B.13)$$

because $(1-\eta^2)$ vanishes at both limits. Substitution of Equation (B.13) in Equation (B.12) yields

$$(A_{iK} - A_{jK}) \int_{-1}^1 d\eta M_{jK} M_{iK} = (p_{iK}^2 - p_{jK}^2) \int_{-1}^1 d\eta \eta^2 M_{jK} M_{iK}$$

or

$$\int_{-1}^1 d\eta \eta^2 M_{jK} M_{iK} = \frac{A_{jK} - A_{iK}}{p_{jK}^2 - p_{iK}^2} \int_{-1}^1 d\eta M_{jK} M_{iK}, \quad j \neq i. \quad (B.14)$$

This result implies that the "inner" functions $M_{iK}(\eta, r_n)$ and $M_{jK}(\eta, r_n)$ are orthogonal only for the special case in which $p_{iK}^2 = p_{jK}^2$ and $A_{iK} \neq A_{jK}$. Equation (B.14) does, however, provide a useful check of numerical integration.

An "outer" function $\Lambda_{iK}(\xi, r_n)$, having $K \neq K$, obeys the differential equation (Bates, Ledsham, and Stewart, 1953):

$$\frac{d}{d\xi} \left\{ (\xi^2 - 1) \frac{d\Lambda_{iK}}{d\xi} \right\} + \left\{ \Lambda_{iK} + 2r_n \xi - p_{iK}^2 \xi^2 - \frac{K^2}{\xi^2 - 1} \right\} \Lambda_{iK} = 0. \quad (B.15)$$

A different "outer" function $\Lambda_{jK}(\xi, r_n)$, which has the same value of K , obeys the differential equation

$$\frac{d}{d\xi} \left\{ (\xi^2 - 1) \frac{d\Lambda_{jK}}{d\xi} \right\} + \left\{ \Lambda_{jK} + 2r_n \xi - p_{jK}^2 \xi^2 - \frac{K^2}{\xi^2 - 1} \right\} \Lambda_{jK} = 0. \quad (B.16)$$

Multiplication Equation (B.15) by Λ_{jK} and Equation (B.16) by Λ_{iK} , subtraction of the two, and integration over $d\xi$ yields

$$\begin{aligned} & \int_1^\infty d\xi \left\{ \Lambda_{jK} \frac{d}{d\xi} (\xi^2 - 1) \frac{d\Lambda_{iK}}{d\xi} - \Lambda_{iK} \frac{d}{d\xi} (\xi^2 - 1) \frac{d\Lambda_{jK}}{d\xi} \right\} \\ &= - (\Lambda_{iK} - \Lambda_{jK}) \int_1^\infty d\xi \Lambda_{jK} \Lambda_{iK} \\ &+ (p_{iK}^2 - p_{jK}^2) \int_1^\infty d\xi \xi^2 \Lambda_{jK} \Lambda_{iK}. \end{aligned} \quad (B.17)$$

Integration by parts yields

$$\begin{aligned} & \int_1^\infty d\xi \left\{ \Lambda_{jK} \frac{d}{d\xi} (\xi^2 - 1) \frac{d\Lambda_{iK}}{d\xi} \right\} = - \int d\xi (\xi^2 - 1) \frac{d\Lambda_{jK}}{d\xi} \frac{d\Lambda_{iK}}{d\xi} \\ &= \int_1^\infty d\xi \Lambda_{iK} \frac{d}{d\xi} (\xi^2 - 1) \frac{d\Lambda_{jK}}{d\xi}, \end{aligned} \quad (B.18)$$

because at the upper limit $\Lambda_{jK}(\xi, r_n) \xrightarrow[\xi \rightarrow \infty]{} 0$ and $\Lambda_{iK}(\xi, r_n) \xrightarrow[\xi \rightarrow \infty]{} 0$

and at the lower limit $(\xi^2 - 1)$ vanishes at $\xi = 1$. Substitution of Equation (B.18) in Equation (B.17) yields

$$\int_1^\infty d\xi \xi^2 \Lambda_{jK} \Lambda_{iK} = \frac{\Lambda_{jK} - \Lambda_{iK}}{p_{jK}^2 - p_{iK}^2} \int_1^\infty d\xi \Lambda_{jK} \Lambda_{iK}, \quad j \neq i. \quad (B.19)$$

a result similar to Equation (B.14). Equation (B.19) implies that the "outer" functions $\Lambda_{iK}(\xi, r_n)$ and $\Lambda_{jK}(\xi, r_n)$ are orthogonal only for the special case in which $p_{iK}^2 = p_{jK}^2$ and $\Lambda_{iK} \neq \Lambda_{jK}$. Again, Equation (B.19) provides a useful check of numerical integration.

Consider now the product $\Lambda_{iK}(\xi, r_n) \cdot M_{iK}(n, r_n)$ and the similar product $\Lambda_{jK}(\xi, r_n) \cdot M_{jK}(n, r_n)$. Multiplication of these two products together and integration over the (ξ, n) volume element $(\xi^2 - n^2) d\xi dn$ yields

$$\begin{aligned}
 & \int_1^\infty d\xi \int_{-1}^1 dn (\xi^2 - n^2) (\Lambda_{jK} M_{jK}) (\Lambda_{iK} M_{iK}) \\
 &= \int_1^\infty d\xi \xi^2 \Lambda_{jK} \Lambda_{iK} \cdot \int_{-1}^1 dn M_{jK} M_{iK} - \int_1^\infty d\xi \Lambda_{jK} \Lambda_{iK} \int_{-1}^1 dn n^2 M_{jK} M_{iK} \\
 &= \left(\frac{\Lambda_{jK}^2 - \Lambda_{iK}^2}{p_{jK}^2 - p_{iK}^2} - \frac{\Lambda_{jK} - \Lambda_{iK}}{p_{jK}^2 - p_{iK}^2} \right) \int_1^\infty d\xi \Lambda_{jK} \Lambda_{iK} \int_{-1}^1 dn M_{jK} M_{iK} \\
 &= 0, \quad j \neq i.
 \end{aligned} \tag{B.20}$$

in which Equations (B.14) and (3.19) have been used. This result checks Equation (B.9) above, because for $K = K$ and $j \neq i$ Equation (B.9) becomes

$$\begin{aligned}
 0 &= \int_1^\infty d\xi \int_{-1}^1 dn (\xi^2 - n^2) F_{jK} F_{iK} \\
 &= \mathcal{N}_{jK} \mathcal{N}_{iK} \int_1^\infty d\xi \int_{-1}^1 dn (\xi^2 - n^2) (\Lambda_{jK} M_{jK}) (\Lambda_{iK} M_{iK}), \quad j \neq i.
 \end{aligned}$$

Cancellation of the normalization constants yields the same result as Equation (B.20). Thus, in spite of the lack of orthogonality of the functions $\Lambda_{iK}(\xi, r_n)$ and $\Lambda_{jK}(\xi, r_n)$ or $M_{iK}(n, r_n)$ and $M_{jK}(n, r_n)$ separately, the paired functions $\Lambda_{iK}(\xi, r_n) M_{iK}(n, r_n)$ are orthogonal to $\Lambda_{jK}(\xi, r_n) M_{jK}(n, r_n)$ with respect to the weight function $(\xi^2 - n^2)$.

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