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FOCK'S REPRESENTATION FOR MOLECULAR ORBITALS

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by
Tai-ichi Shibuya
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PREFACE

The motion of an electron in a Coulombic field of atoms or molecules is given by the Schrödinger equation. The equation has a differential equation form in ordinary position space, while in momentum space, which is the canonical conjugate space of position space, it has an integral equation form. It is usual to solve the Schrödinger equation in position space, since in practice a differential equation is usually easier to handle than an integral equation.

There are, however, some mathematical physicists who have studied the equation in momentum space. V. Fock is particularly outstanding among them. In the present thesis, Fock's work is extended. In his study of the hydrogen atom Fock solved the integral equation by projecting the 3-dimensional momentum space onto the 4-dimensional hypersphere in the way of projective geometry. Then after symmetrizing the integral equation he reduced it to an eigenvalue problem for the R_4 spherical harmonics. He obtained the eigenenergies of the hydrogen atom very elegantly and also explained the so-called "accidental" degeneracy problem of the hydrogen atom purely mathematically.

In Chapter I of this thesis, the one-center (Kepler) problem in 2-dimensional momentum space is discussed in the same way as Fock did for the hydrogen atom problem.

For many years Fock's work has remained a curiousity because of its mathematical difficulty, and because little has been known about the R_4 spherical harmonics. However recently L. C. Biedenharn has done

much to remove this trouble. In Chapter II of this thesis, by the use of his results it is shown that the one-electron many-center problem is nicely formulated in terms of the R_4 spherical harmonics. Also some approximation problems are discussed.

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CHAPTER I

THE KEPLER PROBLEM IN TWO-DIMENSIONAL MOMENTUM SPACE

ABSTRACT

V. Fock studied the hydrogen atom problem in momentum space by projecting the space onto a 4-dimensional hyper-sphere. He found that as a consequence of the symmetry of the problem in this space the eigenfunctions are the R_4 spherical harmonics and that the eigenvalues are determined only by the principal quantum number n. In this chapter we note that if his method is applied to the 2-dimensional Kepler problem in momentum space, the eigenfunctions are the R_3 spherical harmonics, $Y_{\underline{lm}}$, and the eigenvalues are determined only by the quantum number l. These facts enable one to give a visualizable geometrical discussion of the dynamical degeneracy.

INTRODUCTION

A geometrical illustration of a dinamical symmetry is often a great aid to the understanding. We have found that a 2-dimensional analog of Fock's treatment of the "accidental" degeneracy and "extra" symmetry of the hydrogen atom$^{(1)}$ is particularly helpful in this regard.

Fock began his discussion of the dinamical symmetry of the hydrogen atom with the momentum space Schrödinger (integral) equation for the atom. He made a change of the independent variables in this equation and then redefined his dependent variables to symmetrize the integral equation. We proceed analogously for a corresponding 2-dimensional problem.

I-1. FOCK TREATMENT OF THE TWO-DIMENSIONAL KEPLER PROBLEM

The Schrödinger equation for an electron in the potential, $V(\vec{r})$, is given in Hartree's atomic units by

$$(2E + \nabla^2)\, u(\vec{r}) = 2V(\vec{r})\, u(\vec{r}), \tag{I-1}$$

where $\vec{r}$ is the position vector of the electron, $u(\vec{r})$ the wave function, E the electronic energy associated with $u(\vec{r})$, and ∇^2 the Laplace operator for the electron. This position space equation may be Fourier-transformed into a momentum space equation, which in the 2-dimensional case is:

$$(p_o^2 + p^2)\, \phi(\vec{p}) = -2\int V'(\vec{p}-\vec{p}\,')\, \phi(\vec{p}\,')\, d^2p'. \tag{I-2}$$

The corresponding equation in the 3-dimensional case is formally the same if d^2p is changed to d^3p. In equation (I-2),

$$p_o^2 = -2E, \tag{I-3}$$

$$\phi(\vec{p}) = (2\pi)^{-1}\int e^{-i\vec{p}\cdot\vec{r}}\, u(\vec{r})\, d^2r \;; \qquad u(\vec{r}) = (2\pi)^{-1}\int e^{i\vec{p}\cdot\vec{r}}\, \phi(\vec{p})\, d^2p\,, \tag{I-4}$$

and

$$V'(\vec{p}) = (2\pi)^{-2}\int e^{-i\vec{p}\cdot\vec{r}}\, V(\vec{r})\, d^2r \;; \qquad V(\vec{r}) = \int e^{i\vec{p}\cdot\vec{r}}\, V'(\vec{p})\, d^2p. \tag{I-5}$$

Analogous equations hold in the 3-dimensional problem if $2\pi \longrightarrow (2\pi)^{3/2}$ and $d^2 \longrightarrow d^3$.

As shown in the Appendix of this chapter, if the 2-dimensional potential is "Coulombic", that is,

$$V(\vec{r}) = -Z/r, \tag{I-6}$$

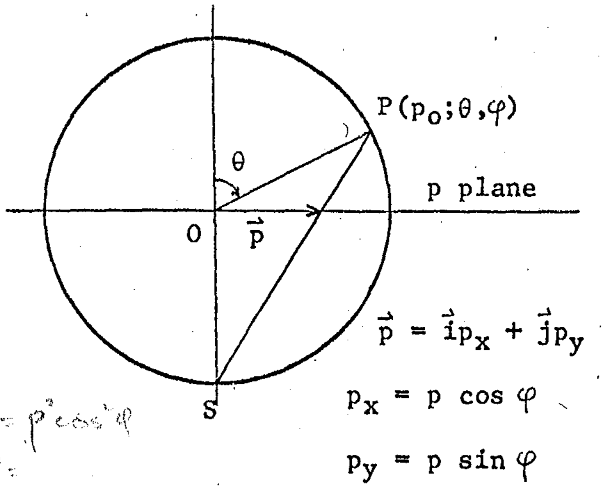
where Z is the charge of the center, then

$$V'(\vec{p}) = -Z/(2\pi p). \tag{I-7}$$

Substitution of (I-7) into (I-2) gives

$$(p_o^2 + p^2)\, \phi(\vec{p}) = \frac{Z}{\pi}\int \frac{1}{|\vec{p}-\vec{p}\,'|}\, \phi(\vec{p}\,')\, d^2p'. \tag{I-8}$$

Now we may project the 2-dimensional momentum space onto the 3-dimensional sphere of radius p_o in the same way that Fock did for the 3-dimensional momentum space problem. A sphere is drawn around the origin of the p space so that the center of the sphere coincides with the origin. The projective origin is taken at the south pole S. Then a vector $\vec{p}$, whose components are p_x, p_y, is projected onto the sphere where it may be described as $(p_o;\theta,\varphi)$ using ordinary spherical polar coordinates. From Figure I-1, we find that, for this stereographic projection,



$\vec{p} = \vec{i}p_x + \vec{j}p_y$

$p_x = p\cos\varphi$

$p_y = p\sin\varphi$

$p_x^2 = p^2\cos^2\varphi$
$p_y^2 =$

FIGURE I-1.

$$p \longrightarrow p_o \tan\theta/2 \ ; \quad \varphi \longrightarrow \varphi \ . \qquad \text{(I-9)}$$

If the rectangular coodinates of the points $P(p_o;\theta,\varphi)$ are x, y, z in a 3-dimensional Cartesian space with origin at the center of the sphere, then we may define our variables so that:

$$(x/p_o)^2 + (y/p_o)^2 + (z/p_o)^2 = 1, \qquad \text{(I-10)}$$

$$\begin{cases} x/p_o = \sin\theta\cos\varphi = \dfrac{2p_op_x}{p_o^2+p^2} , \\ y/p_o = \sin\theta\sin\varphi = \dfrac{2p_op_y}{p_o^2+p^2} , \\ z/p_o = \cos\theta = \dfrac{p_o^2-p^2}{p_o^2+p^2} . \end{cases} \qquad \text{(I-11)}$$

Let γ be the angle spanned between $P(p_o;\theta,\varphi)$ and $P'(p_o;\theta',\varphi')$ on the surface of the sphere. Then $2p_o \sin\gamma/2$ is the distance between P and P', and

$$\left(2\sin\frac{\gamma}{2}\right)^2 = \left(\frac{x-x'}{p_0}\right)^2 + \left(\frac{y-y'}{p_0}\right)^2 + \left(\frac{z-z'}{p_0}\right)^2$$

$$= \frac{4p_0^2|\vec{p}-\vec{p}'|^2}{(p_0^2+p^2)(p_0^2+p'^2)} . \qquad \text{(I-12)}$$

The area element on the unit sphere is, by the third equation of (I-11),

$$d\Omega \equiv \sin\theta \, d\theta \, d\varphi$$

$$= \left(\frac{2p_0}{p_0^2+p^2}\right)^2 p\,dp\,d\varphi \equiv \left(\frac{2p_0}{p_0^2+p^2}\right)^2 d^2p . \qquad \text{(I-13)}$$

Using (I-12) and (I-13) we can temporarily write equation (I-8) as

$$(p_0^2+p^2)^{3/2}\phi(\vec{p}) = \frac{Z/p_0}{2\pi}\int \frac{1}{2\sin\frac{\gamma}{2}} (p_0^2+p'^2)^{3/2}\phi(\vec{p}')\, d\Omega' . \qquad \text{(I-14)}$$

This is a symmetric integral equation, so that the function $(p_0^2+p^2)^{3/2}\phi(\vec{p})$ may be found as an eigenfunction of the kernel $(2\sin\gamma/2)^{-1}$. Introducing a new function,

$$\psi(\Omega) \equiv (\sqrt{8}\, p_0^2)^{-1}(p_0^2+p^2)^{3/2}\phi(\vec{p}) , \qquad \text{(I-15)}$$

into equation (I-14), we obtain

$$\psi(\Omega) = \frac{Z/p_0}{2\pi}\int \frac{1}{2\sin\frac{\gamma}{2}} \psi(\Omega')\, d\Omega' , \qquad \text{(I-16)}$$

where Ω means the collection of variables θ, φ. In equation (I-15), the factor $(\sqrt{8}\, p_0^2)^{-1}$ is inserted to normalize the function $\psi(\Omega)$ to 1.

It is a well-known result of the theory of homogeneous symmetric integral equations that if one can find an expansion of a kernel $K(\Omega, \Omega')$ as $\sum_n \lambda_n f_n^*(\Omega') f_n(\Omega)$ then the eigenfunctions and eigenvalues of the kernel are $f_n(\Omega)$ and λ_n.⁽²⁾ It is not difficult to find such an expansion for the kernel $(2\sin\gamma/2)^{-1}$: The common expansion of the 3-dimensional Coulomb potential,

$$\frac{1}{|\vec{r}_i-\vec{r}_j|} \equiv \frac{1}{r_{ij}} = \sum_{lm} \frac{r_<^l}{r_>^{l+1}} \cdot \frac{2\pi}{l+\frac{1}{2}} Y_{lm}^*(\Omega') Y_{lm}(\Omega) , \qquad \text{(I-17)}$$

gives on the unit sphere:

$$\left(\frac{1}{r_{ij}}\right)_{r_i=r_j=1} = \frac{1}{2\sin\frac{\chi}{2}} = \sum_{lm} \frac{2\pi}{l+\frac{1}{2}}\, Y^{*}_{lm}(\Omega')\, Y_{lm}(\Omega). \tag{I-18}$$

Thus, if

$$\Psi_{lm}(\Omega) = Y_{lm}(\Omega) \tag{I-19}$$

and

$$(Z/\rho_0)_{lm} = l + \frac{1}{2} \quad \text{or} \quad E_{lm} = -\frac{1}{2}\left(\frac{Z}{l+\frac{1}{2}}\right)^2, \tag{I-20}$$

then equation (I-16) is solved. This may be verified by substitution.

Now, in solutions (I-19) and (I-20), the quantum number m can take all the integral values from -l to l, so that there exist 2l + 1 eigenfunctions which belong to the energy state l: in other words, the degeneracy of the state is 2l + 1. From (I-19) and (I-20) we see that the ground state wave function is

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \tag{I-21}$$

and the first excited state wave functions are either

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\,\frac{z}{\rho_0}\,; \quad Y_{1\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi} \tag{I-22}$$

or any linear combinations, such as the real functions:

$$\left\{\begin{aligned} \frac{1}{\sqrt{2}}\left[Y_{11}+Y_{1-1}\right] &= \sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi &&= \sqrt{\frac{3}{4\pi}}\,\frac{x}{\rho_0}, \\ \frac{-i}{\sqrt{2}}\left[Y_{11}-Y_{1-1}\right] &= \sqrt{\frac{3}{4\pi}}\sin\theta\sin\varphi &&= \sqrt{\frac{3}{4\pi}}\,\frac{y}{\rho_0}, \\ Y_{10} &= \sqrt{\frac{3}{4\pi}}\cos\theta &&= \sqrt{\frac{3}{4\pi}}\,\frac{z}{\rho_0}. \end{aligned}\right. \tag{I-23}$$

The momentum space wave functions corresponding to the equations of (I-21) and (I-23) are, respectively,

$$\phi_{00} = \sqrt{\frac{2}{\pi}}\,\rho_0^2\,(\rho_0^2+p^2)^{-3/2} \tag{I-24}$$

and

$$\begin{cases} \frac{1}{\sqrt{2}}[\phi_{11}+\phi_{1-1}] = \sqrt{\frac{6}{\pi}}\, p_0^2 (p_0^2+p^2)^{-5/2}\, 2p_0 p_x\,, \\ \frac{-i}{\sqrt{2}}[\phi_{11}-\phi_{1-1}] = -\sqrt{\frac{6}{\pi}}\, p_0^2 (p_0^2+p^2)^{-5/2}\, 2p_0 p_y\,, \\ \phi_{10} = \sqrt{\frac{6}{\pi}}\, p_0^2 (p_0^2+p^2)^{-5/2} (p_0^2-p^2)\,. \end{cases} \qquad \text{(I-25)}$$

The position space wave functions corresponding to these functions in momentum space or in Fock's projective space may be obtained by Fourier transformation (using the second equation of (I-4)), or may be found directly as solutions of the position space Schrödinger equation (I-1).

For the 3-dimensional Kepler problem, Fock obtained as the Schrödinger equation in his projective momentum space on the 4-dimensional hyper-sphere:

$$\psi(\Omega_4) = \frac{Z/p_0}{2\pi^2}\int \frac{1}{(2\sin\frac{\omega}{2})^2}\,\psi(\Omega_4')\,d\Omega_4'\,. \qquad \text{(I-26)}$$

Here ω is the angle analogous to γ in (I-12) but now on the 4-dimensional hyper-sphere, so that $2\sin\omega/2$ is the "distance" between two points on the unit hyper-sphere spanned by the angle ω ; Ω_4 is the collection of angular variables α, θ, φ ($p \rightarrow p_0 \tan\alpha/2$, $\theta \rightarrow \theta$, $\varphi \rightarrow \varphi$) for the 4-dimensional hyper-sphere, and $d\Omega_4$ is the "area" element on the hyper-sphere. He solved this equation finding that the eigenfunctions are the R_4 spherical harmonics:

$$\Psi_{nlm}(\Omega_4) = Y_{nlm}(\Omega_4) \equiv A_{nl}(\alpha)\, Y_{lm}(\Omega)\,, \qquad \text{(I-27)}$$

where

$$\int Y^*_{n'l'm'}(\Omega_4)\, Y_{nlm}(\Omega_4)\, d\Omega_4 = \delta_{n'l'm',\,nlm} \qquad \text{(I-28)}$$

and

$$A_{nl}(\alpha) = \frac{\sqrt{\pi/2}\ \sin^l\alpha}{\sqrt{n^2(n^2-1^2)\cdots(n^2-l^2)}}\,\frac{d^{l+1}}{d(\cos\alpha)^{l+1}}\cos n\alpha\,, \qquad \text{(I-29)}$$

and eigenvalues are:

$$(Z/\rho_0)_{nlm} = n \qquad \text{or} \quad E_{nlm} = -\frac{1}{2}(Z/n)^2. \tag{I-30}$$

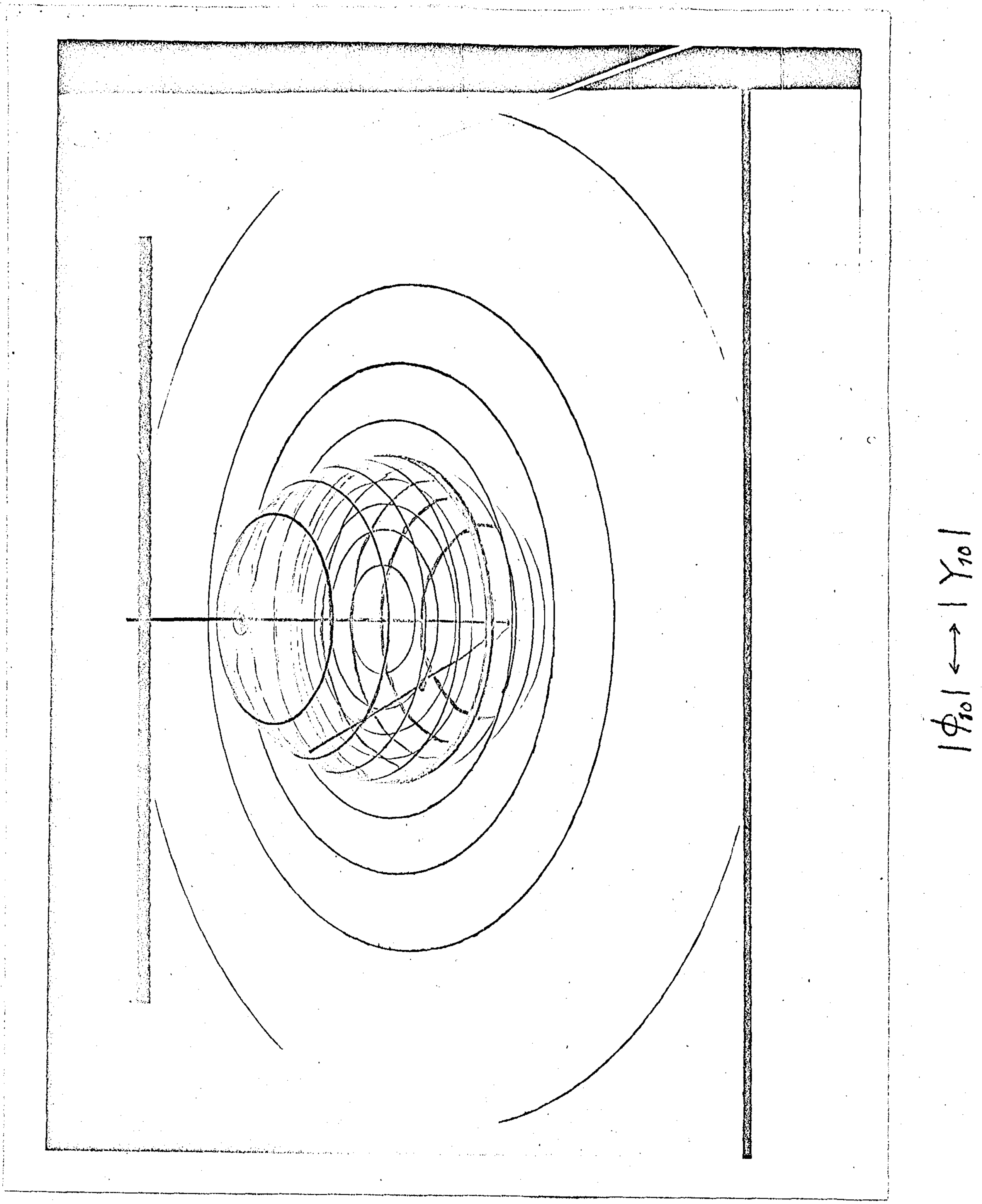
Since the quantum number l can take all the integral values from 0 to n - 1, and the quantum number m from -l to l for each l state, the degeneracy of the energy state n is $\sum_{\ell=0}^{n-1} (2\ell+1) = n^2$.

I-2. DISCUSSION OF THE DEGENERACIES

The degeneracies in the 2- and 3-dimensional Kepler problems arise because, in the 2-dimensional problem the momentum space "potential" has the symmetry of the three dimensional sphere, while, in the 3-dimensional problem, the momentum space "potential" has the symmetry of the 4-dimensional hypersphere. The way in which functions, which are obviously degenerate on the sphere, project into functions, which are obviously different on the plane, is illustrated for the first excited state wave functions of the 2-dimensional problem in Figure I-2.

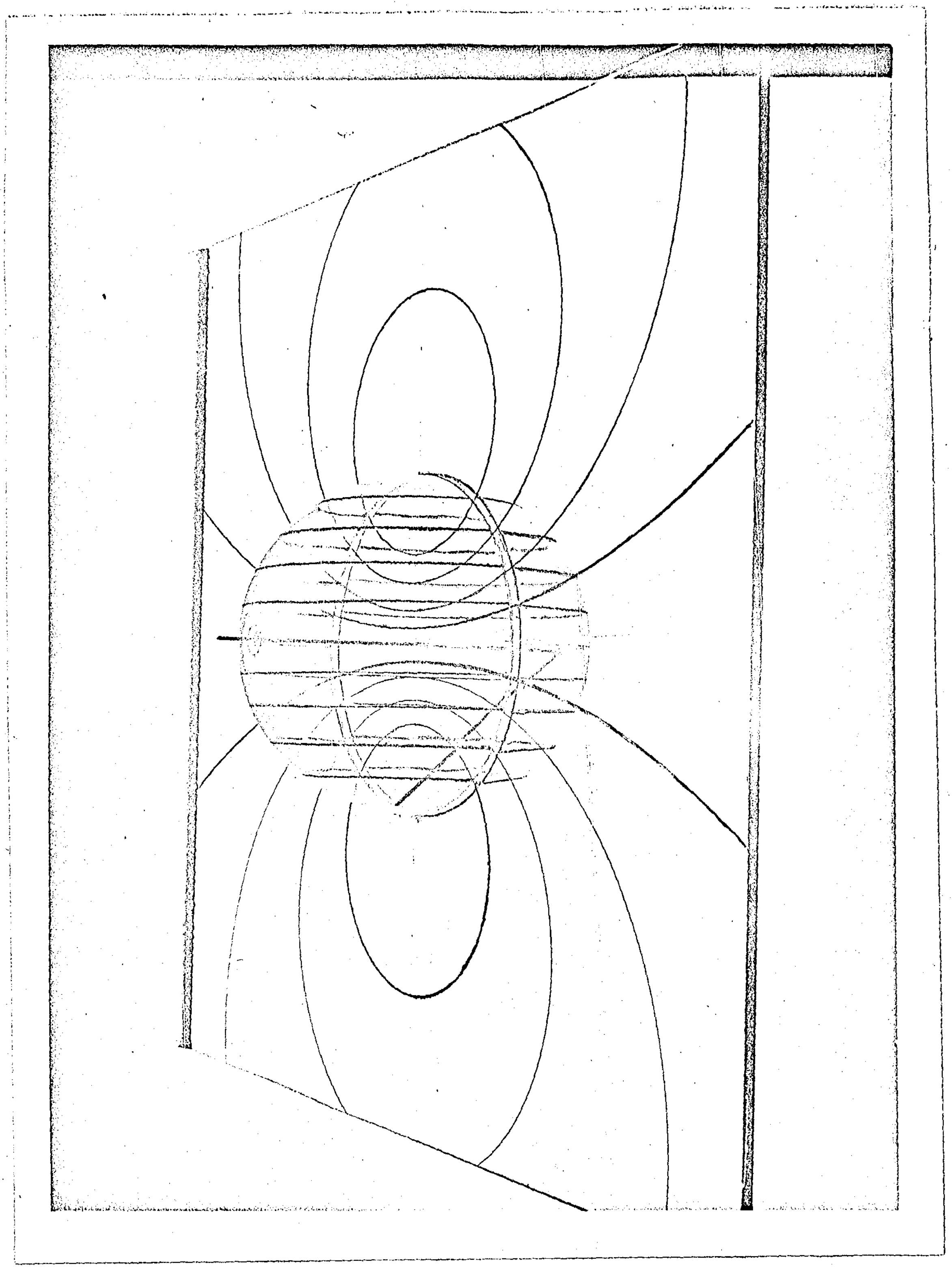
In Figure I-2, photographs (a) and (b) correspond to the cases of the 2-dimensional first excited "s" state, Y_{10}, and the 2-dimensional first excited "p" states, $2^{-\frac{1}{2}} (Y_{11} + Y_{1-1})$ or $-2^{-\frac{1}{2}} (Y_{11} - Y_{1-1})$. Pictures (a) and (b) indicate that in the angular space we can not distinguish one distribution on the sphere from another, since the distributions differ only in orientation. On the other hand the projected functions in the p plane are clearly different. The "s" function has a circular node at the equator of the sphere and the "p" function has a linear node parallel to the x- or y-axis. Photographs (a') and (b') indicate more clearly how the lines on the spheres project into those in the p planes. The lines draw on the nothern hemisphere correspond to those in the p plane inside of the equator of the sphere whose radius is p_o, and the lines on the southern hemisphere correspond to those in the p plane outside of the equator.

Exactly analogous relationships exist for the ordinary hydrogen atom problem.



photograph (a)

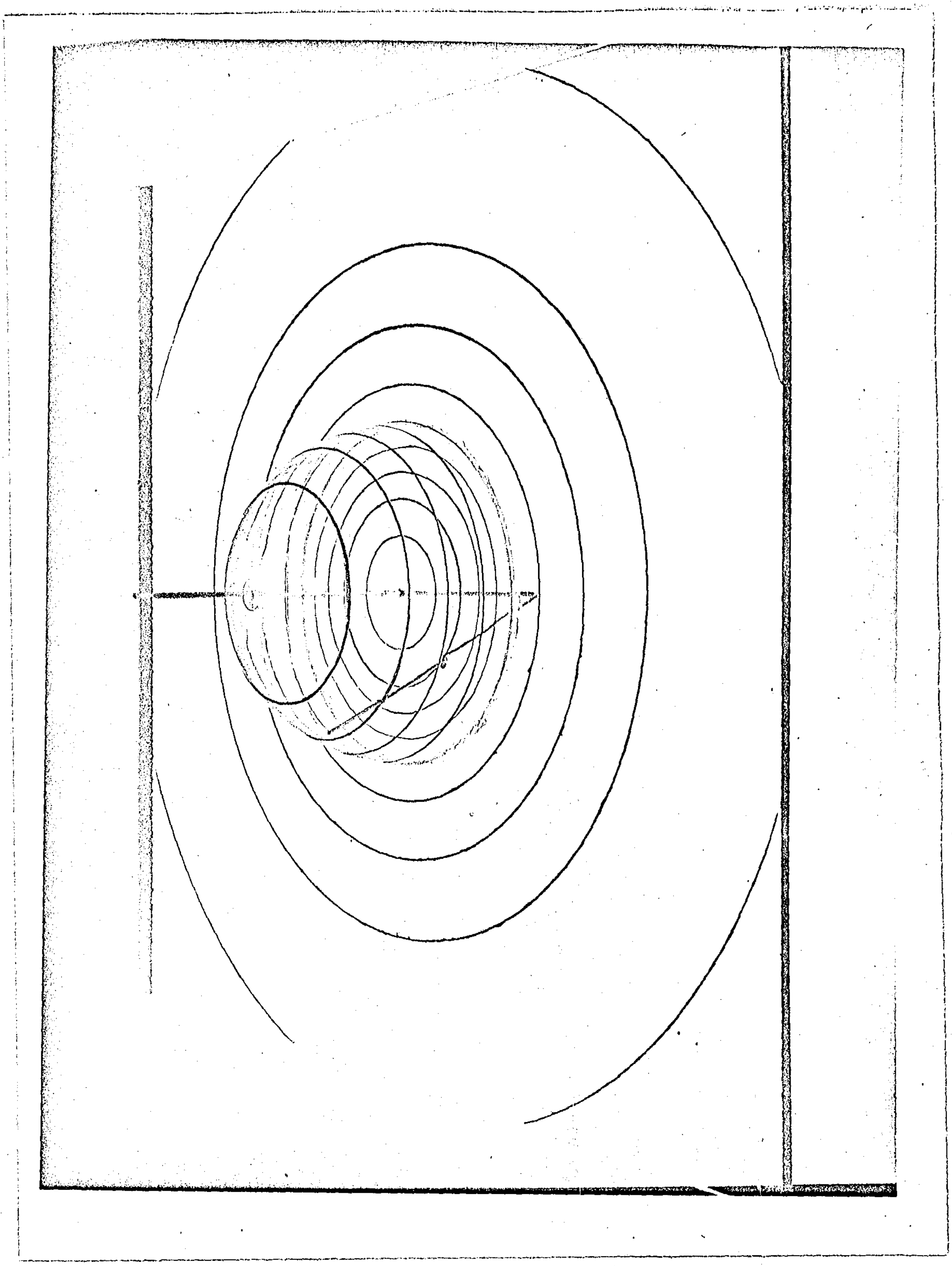
FIGURE I-2.



$$\left|\frac{1}{\sqrt{2}}(\phi_{11} \pm \phi_{1-1})\right| \longleftrightarrow \left|\frac{1}{\sqrt{2}}(Y_{11} \pm Y_{1-1})\right|$$

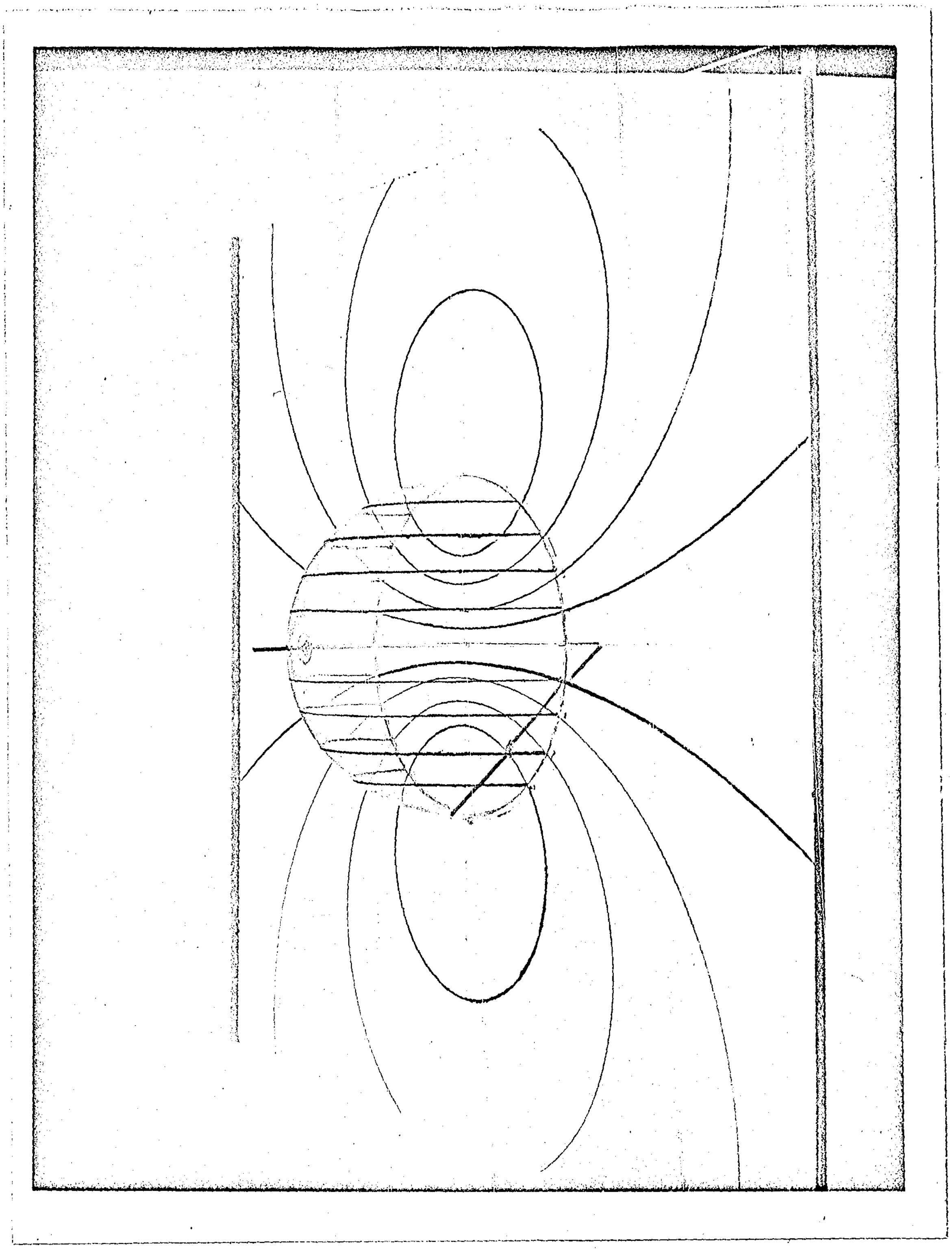
photograph (b)

FIGURE I-2.



photograph (a')

FIGURE I-2.



photograph (b')

FIGURE I-2.

APPENDIX. THE FOURIER TRANSFORMATION OF THE 2-DIMENSIONAL COULOMBIC POTENTIAL

If the potential $V(\vec{r})$ is given, in 2-dimensional position space, by

$$V(\vec{r}) = -\frac{Z}{r}\, e^{-\alpha r},$$

then its Fourier transform $V'(\vec{p})$ in the 2-dimensional momentum space is obtained as follows:

$$\begin{aligned} V'(\vec{p}) &= (2\pi)^{-2}\int e^{-i\vec{p}\cdot\vec{r}}\,\frac{-Z}{r}\, e^{-\alpha r}\, d^2r \\ &= (2\pi)^{-2}(-Z)\int_0^{\infty} dr\; e^{-\alpha r}\int_0^{2\pi} e^{-ipr\cos\theta}\, d\theta\,. \end{aligned}$$

Now

$$\int_0^{2\pi} e^{-ipr\cos\theta}\, d\theta = 2\int_0^{\pi}\cos(pr\cos\theta)\, d\theta = 2\pi J_0(pr). \quad (3)$$

$$\therefore \quad V'(\vec{p}) = (2\pi)^{-1}(-Z)\int_0^{\infty} e^{-\alpha r} J_0(pr)\, dr = \frac{-Z}{2\pi\sqrt{p^2+\alpha^2}}\,. \quad (4)$$

When $\alpha \rightarrow 0$, we have

$$V(\vec{r}) = \frac{-Z}{r}$$

and the Fourier trans form

$$V'(\vec{p}) = \frac{-Z}{2\pi p}\,.$$

CHAPTER II

MOLECULAR ORBITALS IN MOMENTUM SPACE

ABSTRACT

The troublesome problem of developing cusps in ordinary molecular wave functions can be avoided by working with momentum space wave functions, for these have no cusps. The need for continuum wave functions can be eliminated if one works with a hydrogenic basis set in Fock's projective momentum space. This basis set is the set of the R_4 spherical harmonics and, as a consequence, one may obtain, solely by the ordinary angular momentum calculus, algebraic expressions for all the integrals required in the solution of the momentum space Schrödinger equation.

A number of these integrals and a number of R_4 transformation coefficients are tabulated. The method is then applied to several simple united-atom and LCAO wave functions for H_2^+, and ground state energies and corrected wave functions are obtained. It is found in this numerical work that the method is most appropriate at internuclear distances somewhat less than the equilibrium distance. In Fock's representation both LCAO and united-atom approximations become exact as the internuclear distance approaches zero.

The united-atom expansion can be viewed as an eigenvalue equation for the root-mean-square momentum, $p_o = \sqrt{-2E}$. In the molecule, the matrix operator corresponding to p_o is related to the operator for the united-atom, by a sum of unitary transformations, one for each nucleus in the molecule.

INTRODUCTION

Much of our knowledge of the properties of the momentum space wave functions of molecules is due to C. A. Coulson and his co-workers, W. E. Duncanson and R. McWeeny. Coulson and Duncanson(5-8) used the Fourier transforms of atomic wave functions to obtain the momentum space counterparts of a variety of ordinary LCAO and valence bond wave functions. In earlier work, Hicks(9) had investigated the momentum space wave function of the hydrogen molecule, and recently F. M. Glaser(10) has obtained the Fourier transform of Bates' hydrogen molecule-ion wave function(11) for momenta parallel to the bond axis.

Momentum space wave functions have the attractive property that their first derivatives are continuous everywhere. This suggests that it may be possible to approximate them by eigenfunction expansions more readily than is the case for position space wave functions which possess a cusp at each nucleus. In addition LCAO momentum space wave functions have a particularly simple dependence upon the coordinates of the nuclei in a molecule, so that they are well adapted to studies of the effects of changes in nuclear framework.

McWeeny(12,13) investigated the solution of the momentum space integral equation for the hydrogen molecule-ion by Svartholm's modification(14) of Kellog's method. In his study of the first iterative correction to the LCAO function he concluded that, because of the awkwardness of the required integrations, the momentum space approach was not promising.

Recently, however, L. C. Biedenharn(15) has obtained the Wigner coefficients of the R_4 group in terms of those of the R_3 group. This makes it practicable to use Fock's remarkable work on the Kepler problem in momentum space(1) in such a way as to avoid the difficulties McWeeny had to face.

II-1. FOCK'S TRANSFORMATION

The integral equation in momentum space corresponding to Schrödinger's equation is

$$(p_0^2 + p^2)\,\psi(\vec{p}) = \int K\,\psi(\vec{p}\,')\,d^3p'. \tag{II-1}$$

Here

$$p_0^2 = -2E\,;\quad K = \sum_j K_j\,;\quad K_j = \pi^{-2}|\vec{p}-\vec{p}\,'|^{-2} Z_j \exp[-i(\vec{p}-\vec{p}\,')\cdot\vec{R}_j]. \tag{II-2}$$

If $\psi(\vec{p})$ is related to $u(\vec{r})$, the position space wave function, by

$$\psi(\vec{p}) = (2\pi)^{-3/2}\int e^{-i\vec{p}\cdot\vec{r}}\,u(\vec{r})\,d^3r, \tag{II-3}$$

then

$$u(\vec{r}) = (2\pi)^{-3/2}\int e^{i\vec{p}\cdot\vec{r}}\,\psi(\vec{p})\,d^3p. \tag{II-4}$$

One often symmetrizes equation like (II-1) by defining a new function $\psi'(\vec{p})$ which obeys

$$\psi'(\vec{p}) = \Lambda\int K'\,\psi'(\vec{p}\,')\,d^3p'; \tag{II-5}$$

where K' is still a symmetric function of $\vec{p}$ and $\vec{p}\,'$, while Λ is the eigenvalue corresponding to $\psi'(\vec{p})$.

For the Kepler problem Fock in addition made the following transformation of variables:

$$\xi = \frac{2p_0 p_x}{p_0^2+p^2} = \sin\alpha\,\sin\theta\,\cos\varphi \tag{II-6a}$$

$$\eta = \frac{2p_0 p_y}{p_0^2+p^2} = \sin\alpha\,\sin\theta\,\sin\varphi \tag{II-6b}$$

$$\zeta = \frac{2p_0 p_z}{p_0^2+p^2} = \sin\alpha\,\cos\theta \tag{II-6c}$$

$$\chi = \frac{p_0^2-p^2}{p_0^2+p^2} = \cos\alpha. \tag{II-6d}$$

This transformation is analogous to a stereographic projection from a plane onto a sphere, but it is from the 3-dimensional hyper-plane onto the 4-dimensional hyper-sphere, $\xi^2+\eta^2+\zeta^2+\chi^2 = 1$. In terms of the p system of variables, this hyper-sphere has radius $p_0 = \sqrt{-2E}$, so that while in the (ξ, η, ζ, χ) system it is a unit sphere, in the p system its radius depends upon p_0. In terms of a spherical polar coordinate system in 3-dimensional p space the transformation may be symbolized by $p \rightarrow p_0 \tan \alpha/2,\ \theta \rightarrow \theta,\ \varphi \rightarrow \varphi$.

On making the further identifications:

$$d^3p = \left(\frac{p_0^2+p^2}{2p_0}\right)^3 d\Omega\ ; \qquad d\Omega = \sin^2\alpha\ \sin\theta\ d\alpha\, d\theta\, d\varphi, \tag{II-7a,b}$$

$$\Psi(\alpha,\theta,\varphi) = \frac{\pi}{\sqrt{8}}\, p_0^{-5/2}(p_0^2+p^2)^2\, \phi(\vec{p}), \tag{II-7c}$$

and noting that

$$\begin{aligned}\left(2\sin\frac{\omega}{2}\right)^2 &= (\xi-\xi')^2+(\eta-\eta')^2+(\zeta-\zeta')^2+(\chi-\chi')^2 \\ &= \frac{4p_0^2\,|\vec{p}-\vec{p}\,'|^2}{(p_0^2+p^2)(p_0^2+p'^2)},\end{aligned} \tag{II-8}$$

Fock found that for the Kepler problem equation (II-1) becomes

$$\Psi(\alpha,\theta,\varphi) = \frac{Z/p_0}{2\pi^2}\int \frac{1}{\left(2\sin\frac{\omega}{2}\right)^2}\ \Psi(\alpha',\theta',\varphi')\, d\Omega'. \tag{II-9}$$

He identified this as an integral equation for the 4-dimensional spherical harmonics, solved it, finding

$$\Psi(\alpha,\theta,\varphi) = \Psi_{nlm}(\alpha,\theta,\varphi)\ ; \qquad Z/p_0 = n$$

and used it to explain the "accidental" degeneracy of the Kepler problem.

Fock normalized his harmonics to the surface area of the hyper-sphere:

$$\frac{1}{2\pi^2}\int \Psi^{*}_{n'l'm'}(\alpha,\theta,\varphi)\,\Psi_{nlm}(\alpha,\theta,\varphi)\, d\Omega = \delta_{n'l'm',\,nlm}\,. \tag{II-10}$$

From equations (II-7) and (II-8) this is equivalent to having

$$\int \frac{p_0^2+p^2}{2p_0^2}\, \phi^*_{n'l'm'}(\vec{p})\, \phi_{nlm}(\vec{p})\, d^3p = \delta_{n'l'm',nlm} . \qquad \text{(II-11)}$$

The functions $\phi_{nlm}(\vec{p})$ of constant p_0 thus are orthonormal with weight factor $(p_0^2 + p^2)/(2p_0^2)$. In contrast, no weight factor is required for functions of constant $z = np_0$,

$$\psi_{z,nlm}(\vec{p}) = (-)^{n+1}(i)^{l}\frac{\sqrt{8}}{\pi}\, p_0^{5/2}(p_0^2+p^2)^{-2}\, Y_{nlm}(\alpha,\theta,\varphi) \;\; ; \; z = np_0 , \qquad \text{(II-12)}$$

obtainable by Fourier transformation of the hydrogenic-atom position space functions $u_{z,nlm}(\vec{r})$. $\psi_{z,nlm} = \text{F.t.}\, u_{z,nlm}(\vec{r})$

The phase factor $(-)^{n+1}(i)^{l}$ in equation (II-12) is a product of two terms: A factor $(-)^{n-l-1}$ is required because the argument of Fock's Gegenbauer polynomials is the negative of the argument of B. Podolsky and L. Pauling(16). An additional factor of $(-i)^{l}$ obtained by Podolsky and Pauling (after a correction is made for an omission in equation (16) of their paper) was omitted in their abstract and in the Handbuch article of H. A. Bethe and E. E. Salpeter(17).

The relation between the functions of constant z and those of constant p_0 is thus

$$(-)^{n+1}(i)^{l}\, \phi_{nlm}(\vec{p}) = \psi_{np_0,\,nlm}(\vec{p}) . \qquad \text{(II-13)}$$

In order that the projection from p space to angular space shall be onto the same sphere in every case, one must require that p_0 be the same for all $\psi_{z,nlm}(\vec{p})$; i.e., that $z = np_0$. An expansion in terms of Fock's R_4 spherical harmonics consequently corresponds to an expansion in p space using hydrogenic functions with z proportional to n and a weight factor $(p_0^2 + p^2)/(2p_0^2)$. Since the R_4 spherical harmonics constitute a complete set on the unit hypersphere, one need not deal with continuum basis functions if one uses this set.

A number of these functions are listed in Table I.

II-2. THE MANY CENTER PROBLEM

When the general momentum space Schrödinger equation (II-1) is symmetrized and Fock's transformation is applied to it, one obtains:

$$\Psi(\alpha,\theta,\varphi) = \frac{p_0^{-1}}{2\pi^2}\int \frac{\sum_j Z_j \exp[-i(\vec{p}-\vec{p}')\cdot\vec{R}_j]}{4\sin^2\frac{\omega}{2}} \Psi(\alpha',\theta',\varphi')\, d\Omega'. \qquad \text{(II-14)}$$

For simplicity in notation we have written $\exp(-i\vec{p}\cdot\vec{R})$ where it would have been more natural to have expressed things in terms of angular variables. Henceforth, we shall also write Ω for the collection of variables α, θ, φ.

In the position space problem one often seeks an expansion of $u(\vec{r})$ in terms of hydrogenic functions $u_{z,nlm}(\vec{r})$ based on one or several origins, as in united-atom or LCAO expansions. In momentum space this amounts to expanding $\psi(\vec{p})$ in terms of functions $\exp(i\vec{p}\cdot\vec{R})\psi_{z,nlm}(\vec{p})$. Thus we shall seek solutions of equation (II-14) in which $\Psi(\Omega)$ is, in general, expressed in terms of a series of functions $\exp(i\vec{p}\cdot\vec{R})\Psi_{nlm}(\Omega)$. In order to proceed it is necessary to do integrals of the form:

$$I_{nlm}(\Omega,\vec{R}) = \frac{1}{2\pi^2}\int \frac{e^{i\vec{p}'\cdot\vec{R}}}{4\sin^2\frac{\omega}{2}} \Psi_{nlm}(\Omega')\, d\Omega'. \qquad \text{(II-15)}$$

If we let

$$e^{i\vec{p}\cdot\vec{R}}\Psi_{nlm}(\Omega) = \sum_{\nu\lambda\mu} S^{nlm}_{\nu\lambda\mu}(\vec{R})\, \Psi_{\nu\lambda\mu}(\Omega), \qquad \text{(II-16)}$$

then, since the $\Psi_{\nu\lambda\mu}(\Omega)$ are eigenfunctions, with eigenvalues ν, of the kernel $(4\sin^2\frac{\omega}{2})^{-1}$

$$I_{nlm}(\Omega,\vec{R}) = \sum_{\nu\lambda\mu} \frac{1}{\nu} S^{nlm}_{\nu\lambda\mu}(\vec{R})\, \Psi_{\nu\lambda\mu}(\Omega). \qquad \text{(II-17)}$$

To evaluate S we note that from (II-10) and (II-16)

$$S^{nlm}_{\nu\lambda\mu}(\vec{R}) = \frac{1}{2\pi^2}\int e^{i\vec{p}\cdot\vec{R}}\,\Psi^{*}_{\nu\lambda\mu}(\Omega)\,\Psi_{nlm}(\Omega)\,d\Omega . \tag{II-18}$$

Now let

$$e^{-i\vec{p}\cdot\vec{R}} = \sum_{NLM}\alpha_{NLM}\,(p_0^2+p^2)^{-1}\,\Psi_{NLM}(\Omega). \tag{II-19}$$

Then again from (II-11), (II-12) and (II-13)

$$\alpha_{NLM} = (-)^{N+1}(i)^{L}\frac{\sqrt{2}}{\pi}\,p_0^{1/2}\int e^{-i\vec{p}\cdot\vec{R}}\,\psi^{*}_{Np_0,NLM}(\vec{p})\,d^3p. \tag{II-20}$$

Making use of equation (II-4) one finds, after taking complex conjugates,

$$e^{i\vec{p}\cdot\vec{R}} = 4\sqrt{\pi p_0}\sum_{NLM}(-)^{N+L+1}(i)^{L}\,u_{Np_0,NLM}(\vec{R})\,(p_0^2+p^2)^{-1}\,\Psi^{*}_{NLM}(\Omega). \tag{II-21}$$

Substituting (II-21) into (II-18) now gives

$$S^{nlm}_{\nu\lambda\mu}(\vec{R}) = \sum_{NLM}(-)^{N+L+1}(i)^{L}\sqrt{\pi}\,p_0^{-3/2}\,u_{Np_0,NLM}(\vec{R})\,T(nlm;\nu\lambda\mu;NLM). \tag{II-22}$$

The coefficients

$$T(nlm;\nu\lambda\mu;NLM) = \frac{1}{2\pi^2}\int\frac{4p_0^2}{p_0^2+p^2}\,\Psi_{nlm}(\Omega)\,\Psi^{*}_{\nu\lambda\mu}(\Omega)\,\Psi^{*}_{NLM}(\Omega)\,d\Omega \tag{II-23}$$

may be evaluated by ordinary angular momentum algebra because R_4 is locally isomorphic with $R_3 \times R_3$.

The discussion of this evaluation, however, is reserved for the appendix, because in order to obtain the T in this way, it is first necessary to make explicit some results of Biedenharn on the connection between R_4 and R_3 Wigner coefficients. When the evaluation is carried out one finds that, because of the triangle conditions on the angular momentum addition coefficients, the sum of equation (II-22) is restricted to

$$|n-\nu| \le N \le n+\nu\ ; \quad |l-\lambda| \le L \le l+\lambda .$$

The only functions required for the evaluation of S and hence $I_{n\ell m}(\Omega,\vec R)$ are seen to be hydrogen atom position space wave functions $u_{Np_o,NLM}(\vec R)$ and angular momentum addition coefficients. The function $p_o^{-3/2}u_{Np_o,NLM}(\vec R)$ is a dimensionless function of p_oR. A number of the S functions are listed in Table IV.

The function S can be given a simple interpretation in position space. One has

$$S^{n\ell m}_{\nu\lambda\mu}(\vec R) = \frac{1}{2\pi^2}\int e^{i\vec p\cdot\vec R}\,\Psi^*_{\nu\lambda\mu}(\Omega)\,\Psi_{n\ell m}(\Omega)\,d\Omega$$

$$= (-)^{\nu+n}(i)^{\lambda-\ell}\int e^{i\vec p\cdot\vec R}\,\psi^*_{\nu p_o,\nu\lambda\mu}(\vec p)\,\frac{p_o^2+p^2}{2p_o^2}\,\psi_{np_o,n\ell m}(\vec p)\,d^3p. \quad \text{(II-24)}$$

One may view $\exp(i\vec p\cdot\vec R)\,\psi_{\nu p_o,\nu\lambda\mu}(\vec p)$ as the Fourier transform of $u^*_{\nu p_o,\nu\lambda\mu}(\vec r-\vec R)$ and $[(p_o^2+p^2)/(2p_o^2)]\psi_{np_o,n\ell m}(\vec p)$ as the Fourier transform of $[(p_o^2-\nabla^2)/(2p_o^2)]\cdot u_{np_o,nlm}(\vec r)$. Parseval's relation then gives

$$S^{n\ell m}_{\nu\lambda\mu}(\vec R) = (-)^{n+\nu}(i)^{\lambda-\ell}p_o^{-2}\int u^*_{\nu p_o,\nu\lambda\mu}(\vec r-\vec R)\left(-E-\frac{1}{2}\nabla^2\right)u_{np_o,n\ell m}(\vec r)\,d^3r\,. \quad \text{(II-25)}$$

Since the difference between the kinetic and total energy operators is the negative of the potential energy operator $-z/r$, S is proportional to the matrix element of the potential energy between $u_{\nu p_o,\nu\lambda\mu}(\vec r-\vec R)$ and $u_{np_o,nlm}(\vec r)$.

The functions $S^{nlm}_{\nu\lambda\mu}(\vec R)$ are elements of a unitary matrix as may be seen by multiplying equation (II-16) by its complex conjugate and integrating over the hyper-sphere.

II-3. UNITED-ATOM EXPANSION

Let us now rewrite equation (II-14) as

$$p_o\,\Psi(\Omega) = \frac{1}{2\pi^2}\int\frac{\sum_j Z_j\exp[-i(\vec p-\vec p')\cdot\vec R_j]}{4\sin^2\frac{\omega}{2}}\,\Psi(\Omega')\,d\Omega'. \quad \text{(II-26)}$$

Expanding the kernel in terms of R_4 spherical harmonics one has

$$K_j = \frac{Z_j \exp[-i(\vec{p}-\vec{p}\,')\cdot\vec{R}_j]}{4\sin^2\frac{\omega}{2}} = Z_j \sum_{n\ell m} [e^{-i\vec{p}\cdot\vec{R}_j} \mathcal{Y}_{n\ell m}(\Omega)] \frac{1}{n} [e^{-i\vec{p}\,'\cdot\vec{R}_j} \mathcal{Y}_{n\ell m}(\Omega')]^*$$

$$= Z_j \sum_{n\ell m} \sum_{\nu\lambda\mu} \sum_{\nu'\lambda'\mu'} [S^{\nu\lambda\mu}_{n\ell m}(\vec{R}_j)]^* \frac{1}{n} [S^{\nu'\lambda'\mu'}_{n\ell m}(\vec{R}_j)] \mathcal{Y}_{\nu\lambda\mu}(\Omega) \mathcal{Y}^*_{\nu'\lambda'\mu'}(\Omega'). \tag{II-27}$$

Hence, if

$$\mathcal{Y}(\Omega) = \sum_{abc} C_{abc} \mathcal{Y}_{abc}(\Omega), \tag{II-28}$$

then

$$p_0 C_{abc} = \sum_{a'b'c'} P^{a'b'c'}_{abc} C_{a'b'c'}, \tag{II-29}$$

where

$$P^{a'b'c'}_{abc} = \sum_j Z_j W^{a'b'c'}_{abc}(\vec{R}_j) \;;\; W^{a'b'c'}_{abc}(\vec{R}_j) = \sum_{n\ell m} [S^{abc}_{n\ell m}(\vec{R}_j)]^* \frac{1}{n} [S^{a'b'c'}_{n\ell m}(\vec{R}_j)].$$

The resulting secular equations when put in matrix form are therefore:

$$(\mathbb{P} - p_0 \mathbb{I})\,\mathbb{C} = \mathbb{O}. \tag{II-30}$$

Here $\mathbb{P}$ is the matrix of $P^{a'b'c'}_{abc}$, $\mathbb{I}$ the identity matrix, $\mathbb{C}$ the vector matrix of the expansion coefficients in (II-28), and $\mathbb{O}$ the null matrix. If $\mathbb{T}$ is the (diagonal) matrix of (1/n) then these equations may evidently be written as

$$\left(\sum_j Z_j \mathbb{S}_j^{-1} \mathbb{T} \mathbb{S}_j - p_0 \mathbb{I}\right) \mathbb{C} = \mathbb{O}. \tag{II-31}$$

It is a valuable check to notice that the "united atom" expansion (II-28), when transformed into momentum space and then into position space, gives, respectively,

$$\psi(\vec{p}) = \sum_{abc} (-)^{a+b+1} (i)^b C_{abc} \psi_{ap_0,abc}(\vec{p}) \tag{II-32a}$$

and

$$U(\vec{r}) = \sum_{abc} (-)^{a+b+1} (i)^{b}\, C_{abc}\, U_{ap_0,abc}(\vec{r}) . \tag{II-32b}$$

Though the functions $\Psi_{ap_0,abc}(\vec{p})$ and $u_{ap_0,abc}(\vec{r})$ are not orthogonal, they are closely related to orthogonal functions introduced by H. Shull and P.-O. Löwdin in their calculation on helium(18) and then later used by K. M. Howell and H. Shull in their one-center calculation on the hydrogen molecule ion(19). Further discussion of this problem is given in section II-5 and Appendix C.

II-4. SOME FIRST ITERATED WAVE FUNCTIONS FOR H_2^+

To gain some idea of the numerical features of the Fock representation approach, we have applied it briefly to the hydrogen molecule ion. Setting $\vec{R}_1 = -\vec{R}_2 = \vec{R}$ and $Z_1 = Z_2 = 1$, and also letting $\Psi^0(\Omega) = \Psi_{100}(\Omega) = 1$, we may treat equation (II-14) as an iterative scheme for approximating the ground state wave function and root-mean-square momentum p_0. The first iterative function $\Psi^1(\Omega)$ is then

$$\begin{aligned}\Psi^1(\Omega) &= \frac{1}{2\pi^2}\int \frac{2\cos[(\vec{p}-\vec{p}\,')\cdot\vec{R}]}{4\sin^2\frac{\omega}{2}}\, \Psi_{100}(\Omega')\, d\Omega' \\ &= \sum_{\nu\lambda\mu} \left[\frac{1}{\nu} S^{100}_{\nu\lambda\mu}(\vec{R})\, e^{-i\vec{p}\cdot\vec{R}} + \frac{1}{\nu} S^{100}_{\nu\lambda\mu}(-\vec{R})\, e^{i\vec{p}\cdot\vec{R}}\right] \Psi_{\nu\lambda\mu}(\Omega) .\end{aligned} \tag{II-33}$$

At this stage we may view $p_0R = s$ as an arbitrary parameter. (In the corresponding position space problem p_0 becomes the scale parameter in the wave function.) The first iterated function is then a source of information on the appropriateness of the choice of starting function. Now equation (II-33) may be viewed as a sum of LCAO functions $\pm(-)^{\nu+1}(i)^{\lambda}\exp(\pm i\vec{p}\cdot\vec{R})\,\Psi_{\nu\lambda\mu}(\Omega)$ with positive real coefficients $\mp(-)^{\nu+1}(-i)^{\lambda}(1/\nu)S^{100}_{\nu\lambda\mu}(\mp\vec{R})$. Using Table IV we have evaluated these coefficients for $s = \frac{1}{2}$, 1, 2. The results are obtainable from Table V. Since plausible values of p_0 lie in the range $1 \leq p_0 \leq 2$, it is apparent that even at quite small internuclear distances, the first iterate is fairly extensive mixture of LCAO functions when the starting function is a 1s "united atom" function.

We may also determine how the first iterate is built of united-atom functions in Fock space. Making use of identity (II-16) once again transforms (II-33) into

$$\begin{aligned}\Psi^{1}(\Omega) &= \sum_{\alpha\beta\gamma} \sum_{\nu\lambda\mu} \left[S^{\nu\lambda\mu}_{\alpha\beta\gamma}(-\vec{R}) \frac{1}{\nu} S^{100}_{\nu\lambda\mu}(\vec{R}) + S^{\nu\lambda\mu}_{\alpha\beta\gamma}(\vec{R}) \frac{1}{\nu} S^{100}_{\nu\lambda\mu}(-\vec{R}) \right] \Psi_{\alpha\beta\gamma}(\Omega) \\ &= \sum_{\alpha\beta\gamma} \left[W^{100}_{\alpha\beta\gamma}(\vec{R}) + W^{100}_{\alpha\beta\gamma}(-\vec{R}) \right] \Psi_{\alpha\beta\gamma}(\Omega). \qquad \text{(II-34)}\end{aligned}$$

The coefficients of the hydrogenic functions $\Psi_{\alpha\beta\gamma}(\Omega)$ are tabulated in Table VI for the same values of p_0R as in previous paragraph. If the starting function is the LCAO function

$$\left[e^{i\vec{p}\cdot\vec{R}} + e^{-i\vec{p}\cdot\vec{R}} \right] \Psi_{100}(\Omega), \qquad \text{(II-35a)}$$

which corresponds to the position space LCAO function

$$e^{-p_0|\vec{r}-\vec{R}|} + e^{-p_0|\vec{r}+\vec{R}|}, \qquad \text{(II-35b)}$$

then the first iterated function is given by

$$\begin{aligned}\Psi^{1}(\Omega) = \sum_{nlm} \Big[&\frac{1}{n} \left\{ \delta_{nlm,100} + S^{100}_{nlm}(2\vec{R}) \right\} e^{-i\vec{p}\cdot\vec{R}} \\ &+ \frac{1}{n} \left\{ \delta_{nlm,100} + S^{100}_{nlm}(-2\vec{R}) \right\} e^{i\vec{p}\cdot\vec{R}} \Big] \Psi_{nlm}(\Omega). \qquad \text{(II-36)}\end{aligned}$$

When $p_0R = 1$, as in the simple LCAO model of the hydrogen molecule ion, one finds that in the first iterated wave function the coefficients of various LCAO functions are as indicated in Table VII.

II-5. ESTIMATION OF ENERGIES OF SOME H_2^+ WAVE FUNCTIONS

There are a number of ways in which Fock representation wave functions may be used to estimate energies. In each of these one treats $s = p_0 R$ as a parameter and calculates the value of p_0 corresponding to a particular value of s. One then may evaluate the corresponding value of $R = s/p_0$.

In Kellog's method, the first approximate eigenvalue is given by

$$p_0 = \left[\langle \Psi^1(\Omega) | \Psi^1(\Omega) \rangle \div \langle \Psi^0(\Omega) | \Psi^0(\Omega) \rangle\right]^{1/2}.$$

Using a united-atom 1s function $\Psi_{100}(\Omega)$ for $\Psi^0(\Omega)$, choosing the small value $s = \frac{1}{2}$ appropriate to such a function, and using the approximate W values of Table VI, one finds the approximation $-2E = p_0^2 = 3.228$ at $R = 0.278$. This energy value is 5.0% higher (or smaller) than Bates' value for an internuclear distance of $2R = 2 \times 0.278 = 0.557$.

In Svartholm's method the first approximate eigenvalue is given by

$$p_0 = \langle \Psi^1(\Omega) | \Psi^0(\Omega) \rangle \div \langle \Psi^0(\Omega) | \Psi^0(\Omega) \rangle .$$

Using the same starting function, and s and W values as in previous paragraph one finds the approximation $-2E = p_0^2 = 3.166$ at an internuclear distance 0.562, a value for the energy 6.6% higher than Bates' value.

If one uses the exact value of $2W_{100}^{100}(\vec{R})$ for $s = \frac{1}{2}$, 1.7924 (Footnote of Table VI), then $-2E \doteq 3.2127$ at an internuclear distance of 0.558. The energy value is 5.4% higher than Bates' value.

The matrix equations (II-30) and (II-31) are identical with the equations one obtains when one uses Ritz' method to approximate the solution of the Schrödinger equation in Fock's representation (II-26). In using Ritz' method, a basis set of n functions leads to a P matrix of dimension n x n. If the elements of this matrix are to be evaluated exactly, one requires an S matrix of dimension $n \times \infty$. Since, both in practice and in principle, this makes little sense, it becomes important to know how truncation of the S matrix affects the calculated values of p_o. We are not in a position to give a general discussion of this question, but we have made a short numerical study of it, using a basis set composed of 1s, 2s, and 3d functions to build the ground state wave function of H_2^+. If S is a 3 x 3 matrix of S_a^b functions in which a and b are each 1s, 2s, 3d, then when $s = \frac{1}{2}$, one obtains an approximate energy, $-2E = 3.055$ at $R = 0.286$. This is higher than Bates' value by 9.6%. If S is enlarged to a 3 x 4 matrix by including S_a^{2p} functions, then for $s = \frac{1}{2}$ one obtains an energy $-2E = 3.276$. This energy is higher than Bates' value by 3.7%. Including S_a^{3s} and S_a^{3p} functions gives a 3 x 6 S matrix which for $s = \frac{1}{2}$ leads to an energy of $-2E = 3.297$ at $R = 0.275$. This is 3.1% higher than Bates' value.

In general, it is not as easy to estimate the energies corresponding to LCAO functions as it is to estimate the energies corresponding to united atom functions. However, it is not difficult to apply Svartholm's method to LCAO functions. One finds that if $\Psi^o(\Omega)$ is the function of equation (II-35a), then when $s = 1$, use of Table VI for $2W_{100}^{100}(2\vec{R})$ gives $-2E = 2.542$ at $R = 0.627$. This is 5.1% higher than Bates' value. If one uses the exact value of $2W_{100}^{100}$ for $s = 1$, viz. 0.9450 (Footnote of Table VI), then $-2E = 2.640$ at $R = 0.616$. This is 2.1% higher than Bates' value. As $R \to 0$, $p_o \to 2$, $(E \to -2)$, and the LCAO function becomes the 1s function appropriate to the helium ion He^+.

In the above paragraph we have shown some simple numerical calculations for H_2^+ using the secular equation in Fock representation (II-30) for some united-atom expansion functions. We have also briefly discussed the truncation problem involved in the S matrix when we evaluate the P matrix. In the procedure for the estimation of the energy we first obtained p_o as an eigenvalue of the operator P from the equation $|\mathbb{P} - p_o \mathbb{I}| = 0$, and then found the energy E from the value of p_o by the relation $p_o^2 = -2E$. Since $\mathbb{C}$ is an eigenvector of P, the expansion coefficients in (II-30) are, in fact, associated with the eigenvalue p_o.

On the other hand, if we apply the variation method to an equivalent expansion function in position space representation (II-32b) and obtain the energy minimized with respect to the expansion coefficients, then the energy is found as a function of p_o, and may be finally minimized with respect to the parameter p_o. In this case the expansion coefficients are associated directly with the energy. At the final point where the energy is minimized with respect to the parameter p_o, the energy value and the parameter value may not be related by the relation $p_o^2 = -2E$.

To compare the two approaches we refer to the numerical work of K. M. Howell and H. Shull$^{(19)}$. In their one-center calculations on H_2^+ they used orthogonal basis functions $\langle n\ell \rangle Y_{\ell m}(\theta,\varphi)$, which form a complete set, introduced by H. Shull and P.-O. Löwdin$^{(18)}$. As shown in Appendix C, the basis functions in (II-32b) $u_{np_o,n\ell m}(\vec{r})$ are closely related to their basis functions. And in fact both basis functions span the same space if we take the same number of them successively from $n\ell = (\ell + 1)\ell$ for each ℓ. All functions used by Howell and Shull are composed of a series of such successive basis functions. Therefore, exactly the same arguments can be applied to our one-center expansion functions in position space representation (II-32b) if we replace their parameter η by p_o.

In Figure II-1 are shown photographs of Howell and Shull's figures in which they show relations of energy values E to the parameter values $\xi = \eta R_{ab}$ for various one-center expansion functions at an internuclear distance $R_{ab} = 2$. Under the figures is shown a table, also from the same article, in which are tabulated basis functions used in their calculations, the parameter values which give the minimum energy values, and the minimum energies. In the table we also add a column for $(\sqrt{-2E})R_{ab}$, in which all the values were evaluated by us from their energy values.

From the table we see that the values of $(\sqrt{-2E})R_{ab}$ are all about 2.85 for the functions composed only of $\langle s \rangle$ basis functions ("spherical approximation"), except a function composed only of $\langle 1s \rangle$. For these functions we see, in Fig.1 of Figure II-1, that the energy values for this parameter value, 2.85, are slightly higher than the minimum energy values, but that the differences are at largest only 0.3 to 0.4%. Thus, we may conclude that as far as the "spherical approximation" is concerned, finding the energy from an eigenvalue p_o by the relation $p_o^2 = -2E$ is fairly exact, except in the case that the wave function is approximated only by a $\langle 1s \rangle$ function.

Similar arguments may be applied to other approximate functions than the "spherical approximation," though the arguments can not be so clear as in the case of the spherical approximation, because Howell and Shull show the effects of the parameters on the energy values separately for $\langle s \rangle$ terms, $\langle d \rangle$ terms, and a $\langle g \rangle$ term.

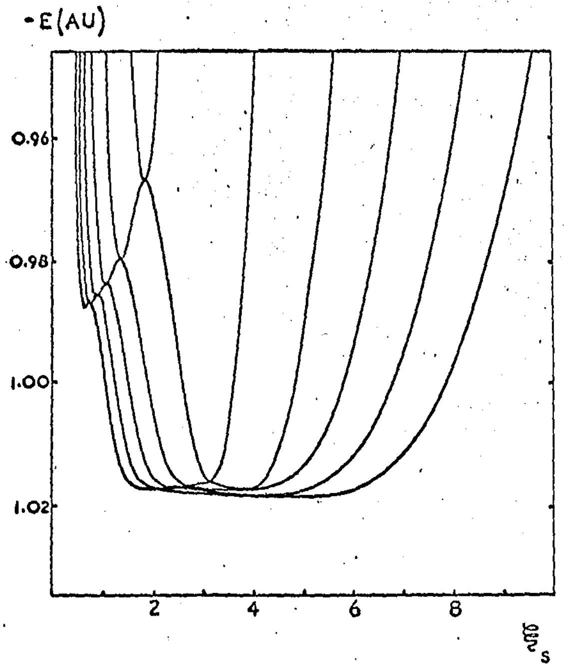


FIG. 1. Energy of the lowest root of the ith order matrix for H_2^+ containing only $\langle s \rangle$ functions as a function of scale parameter $\xi_s = \eta_s R_{ab}$; $R_{ab} = 2$ a.u. Here, $i = 1, 2, \cdots, 6$. E is the total electronic energy in Hartree atomic units.

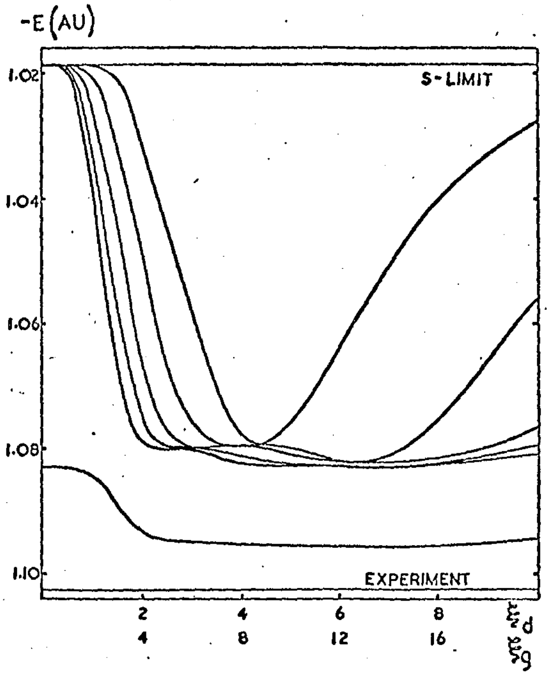


FIG. 2. Energy of lowest root of the matrices for H_2^+ containing six $\langle s \rangle$ functions with $\xi_s = 5.0$ and $i\ \langle d \rangle$ functions; $i = 1, 2, \cdots, 5$ as a function of $\xi_d = \eta_d R_{ab}$; $R_{ab} = 2$ a.u. Also shown is the variation of the lowest root of a 15th order matrix containing six $\langle s \rangle$ functions with $\xi_s = 5.0$, five $\langle d \rangle$ functions with $\xi_d = 7.0$, and four $\langle g \rangle$ functions as a function of $\xi_g = \eta_g R_{ab}$; $R_{ab} = 2$ a.u. E is the total electronic energy in Hartree atomic units.

Matrix size	Functions included	ξ_s	ξ_d	ξ_g	-E	$(\sqrt{-2E})R_{ab}$
1	1s	1.824			0.96732	2.782
2	2s	3.102			1.01617	2.851
3	3s	3.827			1.01744	2.853
4	4s	3.827			1.01743	2.853
5	5s	3.961			1.01832	2.854
6	6s	4.989			1.01842	2.854
7	6s + 1d	5.000	4.397		1.07947	2.939
8	6s + 2d	5.000	6.346		1.08239	2.943
9	6s + 3d	5.000	6.351		1.08230	2.942
10	6s + 4d	5.000	5.309		1.08288	2.943
11	6s + 5d	5.000	7.254		1.08330	2.943
15	6s + 5d + 4g	5.000	7.000	13.59	1.09563	2.961

FIGURE II-1

APPENDIX A. EXPANSION OF PRODUCT OF TWO R_4 SPHERICAL HARMONICS OF THE SAME ARGUMENT

Biedenharn defines$^{(15)}$ R_4 spherical harmonics, Y_{nlm}, with the following properties:

$$\int Y^{*}_{n'l'm'}(\Omega)\, Y_{nlm}(\Omega)\, d\Omega = \delta_{n'l'm',\, nlm} \,, \tag{A1}$$

$$Y^{*}_{nlm}(\Omega) = (-)^{l-m}\, Y_{nl-m}(\Omega) \,. \tag{A2}$$

His phase and nomalization conventions are different from those of Fock so that

$$\Psi^{*}_{nlm}(\Omega) = (i)^{l} \sqrt{2\pi^{2}}\; Y_{nlm}(\Omega) \,. \tag{A3}$$

Note that

$$\Psi^{*}_{nlm}(\Omega) = (-)^{m}\, \Psi_{nl-m}(\Omega) \,. \tag{A4}$$

For the Kronecker product of the rotation matrices of the R_4 group, Biedenharn writes

$$\mathbb{D}^{[p',q']} \cdot \tilde{\mathbb{D}}^{[p,q]} = \sum_{P,Q} U^{\dagger}\, \mathbb{D}^{[P,Q]}\, U \,. \tag{A5}$$

He then shows that the Wigner coefficients of the R_4 group, the matrix elements of U, are

$$\langle p'q'l'm';\, pqlm \,|\, U \,|\, p'q'pq;\, PQLM \rangle = \left[(P+Q-1)(P-Q+1)(2l'+1)(2l+1)\right]^{1/2}$$
$$\times \langle l'lm'm \,|\, l'lLM \rangle \begin{Bmatrix} \frac{1}{2}(p'+q') & \frac{1}{2}(p+q) & \frac{1}{2}(P+Q) \\ \frac{1}{2}(p'-q') & \frac{1}{2}(p-q) & \frac{1}{2}(P-Q) \\ l' & l & L \end{Bmatrix} \,. \tag{A6}$$

Here $\langle l'lm'm | l'lLM \rangle$ is the Wigner coefficient of the R_3 group and the

$\left\{\begin{matrix} - & - & - \\ - & - & - \\ - & - & - \end{matrix}\right\}$ are 9-j coefficients.

In Biedenharn's notation the 4-dimensional spherical harmonics are

$$Y_{nlm}(\Omega) = \frac{n}{\sqrt{2\pi^2}} D^{*[n-1,0]}_{lm,00}(\Omega). \tag{A7}$$

Taking relations (A3) and (A7) into account one obtains

$$\Psi^*_{nlm}(\Omega) = (-i)^l\, n\, D^{[n-1,0]}_{lm,00}(\Omega). \tag{A8}$$

Writing $\bar{n}$ for ½(n - 1) and using equations (A5) and (A6) gives

$$\begin{aligned}\Psi^*_{n'l'm'}(\Omega)\Psi^*_{nlm}(\Omega) &= \sum_{NLM} (i)^{l'+l-L} \frac{n'n}{N} \langle 2\bar{n}'\,0\,l'm';2\bar{n}\,0\,lm|U|2\bar{n}'\,0\,2\bar{n}\,0;2\bar{N}\,0\,LM\rangle \\ &\times \Psi^*_{NLM}(\Omega)\langle 2\bar{n}'\,0\,2\bar{n}\,0;2\bar{N}\,000|U|2\bar{n}'\,000;2\bar{n}\,000\rangle. \end{aligned} \tag{A9}$$

On using relation (A9), taking complex conjugates, noting that all the Wigner and 9-j coefficients are real, and making use of well-known properties of these coefficients, one obtains:

$$\begin{aligned}\Psi_{n'l'm'}(\Omega)\Psi_{nlm}(\Omega) &= \sum_{NLM} (i)^{l'+l-L} [n'nN(2l'+1)(2l+1)]^{1/2} \\ &\times \langle l'l m'm|l'l LM\rangle \left\{\begin{matrix} \bar{n}' & \bar{n} & \bar{N} \\ \bar{n}' & \bar{n} & \bar{N} \\ l' & l & L \end{matrix}\right\} \Psi_{NLM}(\Omega). \end{aligned} \tag{A10}$$

APPENDIX B. EVALUATION OF THE T(nlm;$\nu\lambda\mu$;NLM)

One first notes that

$$\frac{4p_0^2}{p_0^2+p^2} = \frac{4}{1+\tan^2\frac{\alpha}{2}} = 2+2\cos\alpha = 2\Psi_{100}(\Omega) + \Psi_{200}(\Omega). \tag{B1}$$

Equation (II-23) can therefore be written

$$T(nlm;\nu\lambda\mu;NLM) = \frac{1}{2\pi^2}\int[2\Psi_{100}(\Omega)+\Psi_{200}(\Omega)]\Psi_{nlm}(\Omega)\Psi^*_{\nu\lambda\mu}(\Omega)\Psi^*_{NLM}(\Omega)\,d\Omega. \tag{B2}$$

Applying equation (A10) one then obtains the results shown in Table III.

APPENDIX C. THE FUNCTION $u_{np_o,n\ell m}(\vec{r})$

The hydrogen-like wave functions for a nuclear charge z are given by

$$u_{z,n\ell m}(\vec{r}) = R_{z,n\ell}(r)\, Y_{\ell m}(\theta,\varphi);$$

$$n = 1, 2, \ldots; \quad \ell = 0,1,2,\ldots,n-1; \quad m = -\ell,-\ell+1,\ldots,\ell, \tag{C1}$$

where

$$R_{z,n\ell}(r) = -\frac{[(n-\ell-1)!]^{1/2}}{[(n+\ell)!]^{3/2}[2n]^{1/2}}\left(\frac{2z}{n}\right)^{3/2}\left(\frac{2zr}{n}\right)^{\ell} e^{-\frac{zr}{n}}\, \mathcal{L}^{2\ell+1}_{n+\ell}\left(\frac{2zr}{n}\right) \tag{C2}$$

and $Y_{\ell m}(\theta,\varphi)$ are the R_3 spherical harmonics. In (C2), $\mathcal{L}^{2\ell+1}_{n+\ell}$ are the associated Laguerre polynomials defined by$^{(20)}$

$$\mathcal{L}^{2\ell+1}_{n+\ell}(\rho) = -[(n+\ell)!]^2 \sum_{\lambda=0}^{n-\ell-1} \frac{(-\rho)^{\lambda}}{\lambda!\,(n-\ell-1-\lambda)!\,(2\ell+1+\lambda)!} \tag{C3}$$

and

$$\begin{aligned}\mathcal{L}^{2\ell+2}_{n+\ell}(\rho) &= \frac{d}{d\rho}\mathcal{L}^{2\ell+1}_{n+\ell}(\rho)\\ &= [(n+\ell)!]^2 \sum_{\lambda=0}^{n-\ell-2} \frac{(-\rho)^{\lambda}}{\lambda!\,(n-\ell-2-\lambda)!\,(2\ell+2+\lambda)!}\,.\end{aligned} \tag{C4}$$

Substituting $z = np_o$ into (C1) and (C2), we have

$$u_{np_o,n\ell m}(\vec{r}) = R_{np_o,n\ell}(r)\, Y_{\ell m}(\theta,\varphi), \tag{C5}$$

where

$$R_{np_o,n\ell}(r) = -\frac{[(n-\ell-1)!]^{1/2}}{[(n+\ell)!]^{3/2}[2n]^{1/2}}(2p_o)^{3/2}(2p_o r)^{\ell} e^{-p_o r}\, \mathcal{L}^{2\ell+1}_{n+\ell}(2p_o r). \tag{C6}$$

These functions are normalized to 1, but not orthogonal.

H. Shull and P.-O. Löwdin introduced the orthogonal functions$^{(18)}$:

$$\langle n\ell\rangle = \frac{[(n-\ell-1)!]^{1/2}}{[(n+\ell+1)!]^{3/2}}(2\eta)^{3/2}(2\eta r)^{\ell} e^{-\eta r}\, \mathcal{L}^{2\ell+2}_{n+\ell+1}(2\eta r). \tag{C7}$$

These functions were used by K. M. Howell and H. Shull in their one-center calculations for hydrogen molecule ion(19).

Since the polynomials $\mathcal{L}_{n+\ell}^{2\ell+1}(\rho)$ and $\mathcal{L}_{n+\ell+1}^{2\ell+2}(\rho)$ give the same number of terms in the variable ρ for the same values of n and ℓ, and

$$\langle (\ell+1)\ell \rangle = R_{(\ell+1)\eta,(\ell+1)\ell}(r) = \frac{1}{[(2\ell+2)!]^{1/2}} (2\eta)^{3/2} (2\eta r)^{\ell} e^{-\eta r}, \qquad \text{(C8)}$$

we can expand $R_{n\eta,n\ell}(r)$ in terms of $\langle n'\ell \rangle$:

$$R_{n\eta,n\ell}(r) = \sum_{n'=\ell+1}^{n} a_{n,n'} \langle n'\ell \rangle , \qquad \text{(C9)}$$

where the matrix elements $a_{n,n'}$ form a unitary matrix.

Therefore, any vector which is expressed by a basis set $\{\langle (\ell+1)\ell \rangle, \ldots, \langle n\ell \rangle\}$ can be also expressed by a basis set $\{R_{(\ell+1)\eta,(\ell+1)\ell}(r), \ldots, R_{n\eta,n\ell}(r)\}$.

TABLE I. THE SPHERICAL HARMONIC FUNCTIONS $\Psi_{n\ell m}(\alpha, \theta, \varphi)$

nlm	
100	1
200	$2\cos\alpha$
300	$4\cos^2\alpha - 1$
400	$4(2\cos^2\alpha - 1)\ \cos\alpha$
500	$16\cos^4\alpha - 12\cos^2\alpha + 1$
600	$2(4\cos^2\alpha - 1)(4\cos^2\alpha - 3)\ \cos\alpha$
210	$2\sin\alpha\cos\theta$
310	$\sqrt{6}\ \sin 2\alpha\ \cos\theta$
410	$(4/\sqrt{5})\sin\alpha\,(6\cos^2\alpha - 1)\ \cos\theta$
510	$\sqrt{2}\ \sin 2\alpha\ (8\cos^2\alpha - 3)\ \cos\theta$
610	$2\sqrt{3/35}\ \sin\alpha\,(80\cos^4\alpha - 48\cos^2\alpha + 3)\ \cos\theta$
320	$\sqrt{2}\ \sin^2\alpha\ (3\cos^2\theta - 1)$
420	$2\sin\alpha\,\sin 2\alpha\ (3\cos^2\theta - 1)$
520	$\sqrt{10/7}\ \sin^2\alpha\ (8\cos^2\alpha - 1)(3\cos^2\theta - 1)$
620	$4\sqrt{2/7}\ \sin^2\alpha\ (10\cos^2\alpha - 3)\ \cos\alpha\ (3\cos^2\theta - 1)$
430	$(4/\sqrt{5})\sin^3\alpha\ (5\cos^2\theta - 3)\ \cos\theta$
530	$2\sqrt{2}\ \sin^2\alpha\ \sin 2\alpha\ (5\cos^2\theta - 3)\ \cos\theta$
630	$4\sqrt{2/15}\ \sin^3\alpha\ (10\cos^2\alpha - 1)(5\cos^2\theta - 3)\ \cos\theta$
540	$\sqrt{2/7}\ \sin^4\alpha\ (35\cos^4\theta - 30\cos^2\theta + 3)$
640	$2\sqrt{6/7}\ \sin^4\alpha\ \cos\alpha\,(35\cos^4\theta - 30\cos^2\theta + 3)$

TABLE II. REDUCTION OF THE PRODUCT OF THE R_4 SPHERICAL HARMONIC FUNCTIONS*

$$\Psi_{nlm}(\Omega)\,\Psi_{\nu\lambda\mu}(\Omega) = \sum_{NLM} C(nlm;\nu\lambda\mu;NLM)\,\Psi_{NLM}(\Omega)$$

C(100;$\nu\lambda\mu$;NLM)	1				
C(200;200;NLM)	1	1			
C(200;210;NLM)	√(2/3)				
C(200;300;NLM)	1	1			
C(200;310;NLM)	√(2/3)	√(5/6)			
C(200;320;NLM)	1/√2				
C(200;400;NLM)	1	1			
C(200;410;NLM)	√(5/6)	3/√10			
C(200;420;NLM)	1/√2	√(7/10)			
C(200;430;NLM)	√(2/5)				
C(210;210;NLM)	1	-1/3	(2/3)√2		
C(210;300;NLM)	-1/3	(1/3)√5			
C(210;310;NLM)	√(2/3)	-1/√6	√(2/3)		
C(210;320;NLM)	(2/3)√2	-(1/3)√(2/5)	3/√10		
C(300;300;NLM)	1	1	1		
C(300;310;NLM)	1/2	(1/2)√3			
C(300;320;NLM)	-1/2	(1/2)√(7/5)			
C(300;400;NLM)	1	1	1		
C(310;310;NLM)	1	1/2	-1/2	1/√2	√(7/10)
C(310;320;NLM)	1/√2	-(1/5)√(3/2)	(3/5)√(3/2)		
C(310;400;NLM)	-1/√6	√(2/15)	√(7/10))	(8/5) (2/15)	

C(310;410;NLM)	$\sqrt{(5/6)}$ $\quad \sqrt{(2/15)}$ $\quad -\sqrt{(3/10)}$ $\quad (8/5)\sqrt{(2/15)}$ $\quad (2/5)$ $\quad (21/5)$
C(320;320;NLM)	1 $\quad -1/2$ $\quad 1/10$ $\quad 1/\ 2$ $\quad -1/\sqrt{70}$ $\quad (9/5)\sqrt{(2/7)}$
C(320;400;NLM)	$-(2/5)\sqrt{2}$ $\quad (1/5)\sqrt{7}$
C(320;410;NLM)	$-(1/3)\sqrt{(2/5)}$ $\quad (34/75)\sqrt{2}$ $\quad -(1/25)\sqrt{42}$ $\quad -(6/25)\sqrt{2}$ $\quad (9/25)\sqrt{3}$
C(320;420;NLM)	$1/\sqrt{2}$ $\quad -(2/5)\sqrt{2}$ $\quad (1/5)/\sqrt{2}$ $\quad (2/5)\sqrt{2}$ $\quad -(2/5)/\sqrt{7}$ $\quad (6/5)\sqrt{(3/7)}$

*Convention:

The coefficients C(nlm;$\nu\lambda\mu$;NLM) are listed with all those of smallest L first (the smallest N first then larger N), then next smallest L, and so on.

N is restricted by

$$N = |n-\nu| + 1,\ |n-\nu| + 3,\ \ldots,\ n+\nu - 3,\ n+\nu - 1$$

and L is restricted by

$$L = |\ell-\lambda|,\ |\ell-\lambda| + 2,\ \cdots,\ \ell+\lambda-2;\ \ \ell+\lambda,$$

with $M = m + \mu = 0$.

As an example of the use of the table:

$$\Psi_{320}\Psi_{410} = -(1/3)\sqrt{(2/5)}\,\Psi_{210} + (34/75)\sqrt{2}\,\Psi_{410} - (1/25)\sqrt{42}\,\Psi_{610} - (6/25)\sqrt{2}\,\Psi_{430} + (9/25)\sqrt{3}\,\Psi_{630}.$$

Notice that $N > L$.

These C coefficients are $(i)^{\ell+\ell'-L}\sqrt{(n\,n'/N)}$ times the R_4 Wigner coefficients $\langle\ |U|\ \rangle$.

TABLE III. THE COEFFICIENTS $T(nlm;\nu\lambda\mu;NLM)^*$

T(100;100;NLM)	2	1						
T(100;200;NLM)	1	2	1					
T(100;210;NLM)	2	$\sqrt{(2/3)}$						
T(100;300;NLM)	1	2	1					
T(100;310;NLM)	$\sqrt{(2/3)}$	2	$\sqrt{(5/6)}$					
T(100;320;NLM)	2	$1/\sqrt{2}$						
T(100;400;NLM)	1	2	1					
T(100;410;NLM)	$\sqrt{(5/6)}$	2	$3/\sqrt{10}$					
T(100;420;NLM)	$1/\sqrt{2}$	2	$\sqrt{(7/10)}$					
T(100;430;NLM)	2	$\sqrt{(2/5)}$						
T(200;200;NLM)	2	2	2	1				
T(200;210;NLM)	2/3	$2\sqrt{(2/3)}$	$(1/3)\sqrt{5}$					
T(200;300;NLM)	1	2	2	2	1			
T(200;310;NLM)	$2\sqrt{(2/3)}$	3/2	$\sqrt{(10/3)}$	$(1/2)\sqrt{3}$				
T(200;320;NLM)	1/2	$\sqrt{2}$	$(1/2)\sqrt{(7/5)}$					
T(210;210;NLM)	2	2/3	-2/3	-1/3	$(4/3)\sqrt{2}$	2/3		
T(210;300;NLM)	-2/3	$1/\sqrt{6}$	$(2/3)\sqrt{5}$	$1/\sqrt{2}$				
T(210;310;NLM)	$\sqrt{(2/3)}$	$2\sqrt{(2/3)}$	$1/\sqrt{6}$	$-\sqrt{(2/3)}$	$-1/\sqrt{6}$	$1/\sqrt{3}$	$2\sqrt{(2/3)}$	$\sqrt{(7/15)}$
T(210;320;NLM)	$(4/3)\sqrt{2}$	$1/\sqrt{3}$	$-(2/3)\sqrt{(2/5)}$	-1/5	$3\sqrt{(2/5)}$	3/5		

T(300;300;NLM)	$2 \quad 2 \quad 2 \quad 2 \quad 2 \quad 1$
T(300;310;NLM)	$1/\sqrt{6} \quad 1 \quad 7/\sqrt{30} \quad \sqrt{3} \quad \sqrt{(7/10)}$
T(300;320;NLM)	$-1 \quad (1/5)/\sqrt{2} \quad \sqrt{(7/5)} \quad (1/5)\sqrt{7}$
T(310;310;NLM)	$2 \quad 3/2 \quad 1 \quad -1 \quad -1/2 \quad \sqrt{2} \quad 6/5$ $\sqrt{(14/5)} \quad (1/5)\sqrt{14}$
T(310;320;NLM)	$1/\sqrt{3} \quad \sqrt{2} \quad (8/5)/\sqrt{15} \quad -(1/5)\sqrt{6} \quad -(1/5)\sqrt{(7/5)}$ $(3/5)\sqrt{(3/5)} \quad (3/5)\sqrt{6} \quad (9/5)/\sqrt{10}$
T(320;320;NLM)	$2 \quad 1/2 \quad -1 \quad -2/5 \quad 1/5 \quad 1/10 \quad \sqrt{2}$ $2/5 \quad -\sqrt{(2/35)} \quad -(1/5)\sqrt{(2/7)} \quad (18/5)\sqrt{(2/7)}$ $(3/5)\sqrt{(6/7)}$

*Convention:

The coefficients $T(nlm;\nu\lambda\mu;NLM)$ are listed with all those of smallest L first (the smallest N first, then larger N), then next smallest L, and so on.

N is restricted by

$$N = |n-\nu|,\ |n-\nu|+1,\ \ldots,\ n+\nu-1,\ n+\nu$$

and L is restricted by

$$L = |\ell-\lambda|,\ |\ell-\lambda|+2, \cdots, \ell+\lambda-2,\ \ell+\lambda$$

with M = m + = 0.

For example:

$T(210;320;210) = (4/3)\sqrt{2}$ $\qquad$ $T(210;320;310) = 1/\sqrt{3}$

$T(210;320;410) = -(2/3)\sqrt{(2/5)}$ $\qquad$ $T(210;320;510) = -1/5$

$T(210;320;430) = 3\sqrt{(2/5)}$ $\qquad$ $T(210;320;530) = 3/5$

Notice that $N > L$.

TABLE IV. THE FUNCTIONS $S^{nlm}_{\nu\lambda\mu}(\vec{R})$

nlm	$\nu\lambda\mu$	$S^{nlm}_{\nu\lambda\mu}(\vec{R})$	$s = p_oR$
100	100	$(1+s)$ exp-s	
100	200	$(2/3)s^2$ exp-s	
100	210	$i(2/3)s(1+s)$ exp-s	
100	300	$-(1/3)s^2(2-s)$ exp-s	
100	310	$-i(1/\sqrt{6})s(1+s-s^2)$ exp-s	
100	320	$-(1/3)\sqrt{(1/2)}s^2(1+s)$ exp-s	
100	400	$(2/15)s^2(5-5s+s^2)$ exp-s	
100	410	$i(2/75)\sqrt{5}s(5+5s-12s^2+3s^3)$ exp-s	
100	420	$(2/15)s^2(2+2s-s^2)$ exp-s	
100	430	$-i(2/15)\sqrt{(1/5)}s^3(1+s)$ exp-s	
200	200	$(1/3)(3+3s-s^3)$ exp-s	
200	210	$-i(1/3)s(1+s-s^2)$ exp-s	
200	300	$(2/15)s^2(10-5s+s^2)$ exp-s	
200	310	$i(1/5)\sqrt{(2/3)}s(5+5s-4s^2+s^3)$ exp-s	
200	320	$(1/15)\sqrt{2}s^2(2+2s-s^2)$ exp-s	
210	210	$(1/3)(3+3s-s^3)$ exp-s	
210	300	$-i(2/15)s^3(4-s)$ exp-s	
210	310	$(1/5)\sqrt{(2/3)}s^2(3+3s-s^2)$ exp-s	
210	320	$i(1/15)\sqrt{2}s(6+6s+s^2-s^3)$ exp-s	
300	300	$(1/45)(45+45s-60s^2+60s^3-18s^4+2s^5)$ exp-s	
300	310	$-i(1/15)\sqrt{(1/6)}s(15+15s-39s^2+16s^3-2s^4)$ exp-s	

300	320	$-(1/45)\sqrt{(1/2)}\,s^2(3+3s-12s^2+2s^3)\ \mathrm{exp}{-s}$
310	310	$(1/45)(45+45s-18s^2-33s^3+21s^4-3s^5)\ \mathrm{exp}{-s}$
310	320	$-i(1/15)\sqrt{(1/3)}\,s(6+6s-3s^2-5s^3+s^4)\ \mathrm{exp}{-s}$
320	320	$(1/45)(45+45s+6s^2-9s^3-3s^4+s^5)\ \mathrm{exp}{-s}$

TABLE V. THE COEFFICIENTS $(1/\nu)S^{100}_{\nu\lambda\mu}(\pm\vec{R})$

(for $s = p_0 R = \frac{1}{2}, 1, 2$)

$\nu\lambda\mu$	$s = \frac{1}{2}$	$s = 1$	$s = 2$
100	0.9098	0.7358	0.4060
200	0.0505	0.1226	0.1805
210	i 0.1516	i 0.2453	i 0.2707
300	− 0.0253	− 0.0409	0
310	−i 0.0516	−i 0.0501	i 0.0368
320	− 0.0179	− 0.0578	− 0.1276
400	0.0139	0.0123	− 0.0180
410	i 0.0220	−i 0.0055	−i 0.0363
420	0.0139	0.0368	0.0361
430	−i 0.0017	−i 0.0110	−i 0.0484

Note:

$$\left[S^{100}_{\nu\lambda 0}(\vec{R}) \right]^* = S^{100}_{\nu\lambda 0}(-\vec{R}) .$$

TABLE VI. APPROXIMATE COEFFICIENTS $W^{100}_{\alpha\beta\gamma}(\vec{R}) + W^{100}_{\alpha\beta\gamma}(-\vec{R})$ *

$\alpha\beta\gamma$	s = ½	s = 1	s = 2
100	1.7794	1.4288	0.8588
200	0.1866	0.3730	0.4852
210	0	0	0
300	-0.1596	-0.2276	-0.0938
310	0	0	0
320	-0.0376	-0.1006	-0.1212

* Approximated by the first six non-zero terms in their series expansion in $\nu\lambda\mu$, equation (II-34).

It may be shown that

$$W^{100}_{100}(\vec{R}) = \frac{1}{\rho_0}\int \frac{[U_{\rho_0,100}(\vec{r})]^2}{|\vec{r}-\vec{R}|} d^3r = \frac{1}{\rho_0 R}\left[1-(1+\rho_0 R)e^{-2\rho_0 R}\right] \equiv \frac{1}{s}\left[1-(1+s)e^{-2s}\right].$$

Using this one finds that the exact values of $2W^{100}_{100}(\vec{R})$ are 1.7924 (for s = ½), 1.4586 (for s = 1), 0.9450 (for s = 2).

TABLE VII. THE COEFFICIENTS $(1/n)\left[\delta_{nlm,100} + S^{100}_{nlm}(2\vec{R})\right]$

(for $p_oR = 1$)

nlm	
100	1.4060
200	0.1805
210	i 0.2707
300	0
310	i 0.0368
320	– 0.1276
400	– 0.0180
410	–i 0.0363
420	0.0361
430	–i 0.0484

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