Symmetric Euler Angle Decomposition

of the Two-Electron Fixed-Nucleus Problem

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I.   INTRODUCTION

The decomposition of the Laplacian operator,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right),$$

where the coefficient of the second term is proportional to the

square of the angular momentum operator, is the basic relation

between energy and angular momentum in the quantum mechanics of

the one body problem (or the relative motion of two particles).

When acting on a wave function which is an eigenfunction of total

angular momentum ℓ, the Laplacian simplifies to

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2}$$

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in which form it is clear that the effect of this decomposition is

to reduce the Schrödinger equation from a three dimensional partial

differential equation to a one dimensional (ordinary) differential

equation. As such this relation is of fundamental mathematical

importance and is familiar to everyone who utilizes quantum

mechanics at all.

The analogous procedure when more than one particle is

involved, in particular two identical particles in an external

force field, although known, is not as well known, nor is it as

well developed. When the external field is that of a fixed nucleus,

the wave function is expanded in eigenfunctions of the total angular

momentum of the two particles multiplied by functions of the three

remaining independent variables. The total angular momentum eigen-

functions are functions of the three Euler angles only. These angles

are not unique, but in some way they must describe the orientation

of the instantaneous plane formed by the two particles and the center

of coordinates (nucleus) in space. The remaining three coordinates

then describe the positions of the particles in this plane, and the

functions of these variables are the generalized radial functions.

Hylleraas' original papers[1] in effect contained the reduced or

radial equations for total S states in terms of the residual coor-

dinates r_1, r_2, r_{12}. In this case, the total orbital angular

momentum is a constant function, and hence the reduction of a six-

dimensional to a three-dimensional partial differential equation is

independent of how one defines the Euler angles.

The standard treatment of the general problem is due to Breit,[2,3]

He used the Euler angles that Hylleraas[1] originally introduced:

namely the two spherical angles of one of the particles in the space

fixed coordinate system and a second azimuthal angle between the

r_1 - z plane and the r_2-r_1 plane. Breit's remaining coordinates

were chosen as r_1, r_2, and θ_{12}, the latter being the angle between

r_1 and r_2. If, however, one wants to describe two electron atoms or ions in the approximation that the nuclei are fixed, then one has an additional requirement of which there is no analogue in the one-body problem. And that is the Pauli principal: the requirement that the spatial function be either symmetric or antisymmetric under the exchange of the particle coordinates. It is clear that the Hylleraas-Breit choice of Euler angles (which we hereinafter refer to as the Hylleraas-Breit angles), being quite unsymmetrical with respect to the two particles, is not optimum in this respect[4]. In fact the construction of linear combinations of angular momentum functions with the appropriate exchange properties is a very difficult task which depends not only on the Euler angles but on θ_{12} as well. It is not surprising, therefore, that Breit's original work[2] was limited to P-states, and work thereafter has always been limited to specific angular momentum states[5].

However, a treatment by Holmberg[6] using a symmetrical choice of Euler angles (which we shall call Holmberg's angles) has in the interim been carried out. With these angles the description of exchange as well as parity (which latter property is also simply describably with the H-B angles) is simple (although these properties are only alluded to in Holmberg's paper[5]). One of the purposes of the present paper is to examine these properties and relate them more clearly to the construction of the total wave function

and further clarify other aspects of Holmberg's important paper. Principally, however, we shall derive the general radial equations for arbitrary angular momentum (ℓ) for the case of two identical particles in an external field. Holmberg's treatment applies to three particles of the same mass.

It is clear that in treating three particles of equal mass Holmberg had in mind the three nucleon problem whereas we are interested in two-electron atoms, ions, and diatomic molecules. The application of this formalism to two electron atoms and ions is clear, and the decomposition amounts to a rigorous reduction of the Schrödinger equation. It should only be remarked here that the scattering of electrons from one electron atoms and ions is also a special class of these problems. We have therefore worked out the connection between the boundary conditions for electron-atom scattering and Holmberg's angles (Section VIII).

Inasmuch as Holmberg's paper refers to the three nucleon problem, reference should also be made to the papers of Derrick and Blatt[7]. These papers deal much more realistically with the three nucleon problem in that full account is taken of an internucleon potential which is considerably more complicated than a central potential. As regards the actual choice of coordinates, Derrick and Blatt define axes along the moments of inertia of the three-body system. As such they will depend on the lengths of the interparticle distances and therefore are quite different from Holmberg's angles (Section II).

II. HOLMBERG'S ANGLES

Figure 1 contains a perspective drawing of Holmberg's angles which define the particle plane with respect to the space fixed x, y, and z axes. The rotated axes x', y', z' are then defined by

$$\hat{z}' = \frac{\hat{r}_1 \times \hat{r}_2}{|\hat{r}_1 \times \hat{r}_2|} \tag{1}$$

$$\hat{x}' = \frac{\hat{z} \times \hat{z}'}{|\hat{z} \times \hat{z}'|} \tag{2}$$

$$\hat{y}' = \hat{z}' \times \hat{x}' \tag{3}$$

The Holmberg Euler angles are then

$$\theta \equiv \text{angle between } \hat{z} \text{ and } \hat{z}' \tag{4}$$

$$\phi \equiv \text{angle between } \hat{x}' \text{ and } \hat{x} \tag{5}$$

$$\psi \equiv \text{angle between } \hat{x}' \text{ and } (\hat{r}_2 - \hat{r}_1) \tag{6}$$

The ranges and planes of these angles are:

$$0 \leqslant \theta \leqslant \pi \qquad \text{in z-z' plane}$$

$$0 \leqslant \phi \leqslant 2\pi \qquad \text{in x-y plane}$$

$$0 \leqslant \psi \leqslant 2\pi \qquad \text{in x'-y' plane}$$

As is usual a cap on a vector is used to represent a unit vector in the given direction. In particular $\hat{i}$, $\hat{j}$, $\hat{k}$ are the three unit vectors along the (space fixed) x, y, and z axes respectively,

and thus are synonymous with $\hat{x}$, $\hat{y}$, and $\hat{z}$. Similarly $\hat{i}'$, $\hat{j}'$, $\hat{k}'$ and $\hat{x}'$, $\hat{y}'$, $\hat{z}'$ are identical.

It is clear from the figure that $\hat{x}'$, being in the x-y plane has components:

$$\hat{x}' = \hat{i} \cos \phi + \hat{j} \sin \phi \tag{7}$$

Since $\hat{x}'$ is perpendicular to the z-z' plane, it is perpendicular to every line in that plane going through the origin. This includes specifically the line of intersection of the z-z' plane with the x-y plane. However the azimuthal angle of that intersecting line is the azimuth of $\hat{z}'$ itself, and since $\hat{x}'$ has azimuth ϕ, $\hat{z}'$ has azimuth $\frac{3\pi}{2} + \phi$ (cf. figure 1). The polar angle of $\hat{z}'$ is clearly Θ, therefore we have the important relation:

$$\hat{z}' = \hat{i} \sin \theta \sin \phi - \hat{j} \sin \theta \cdot \cos \phi + \hat{k} \cos \theta \tag{8}$$

The relations between Holmberg's angles and the spherical angles of the individual particles are obtained by substituting Eqs. (7) and (8) into the lhs of Eqs. (1) and (2) and using the ordinary decomposition of r_1 and r_2 in the rhs:

$$\hat{r}_1 = \hat{i} \sin \vartheta_1 \cos \varphi_1 + \hat{j} \sin \vartheta_1 \sin \varphi_1 + \hat{k} \cos \vartheta_1$$

$$\hat{r}_2 = \hat{i} \sin \vartheta_2 \cos \varphi_2 + \hat{j} \sin \vartheta_2 \sin \varphi_2 + \hat{k} \cos \vartheta_2 .$$

One obtains

$$\sin \theta_{12} \cos \theta = \sin \vartheta_1 \sin \vartheta_2 \sin(\varphi_2 - \varphi_1) \tag{9}$$

$$\sin \theta_{12} \sin \theta \sin \Phi = \sin \vartheta_1 \sin \varphi_1 \cos \vartheta_2 - \cos \vartheta_1 \sin \vartheta_2 \sin \varphi_2 \tag{10}$$

$$\sin \theta_{12} \sin \theta \cos \Phi = \sin \vartheta_1 \cos \varphi_1 \cos \vartheta_2 - \cos \vartheta_1 \sin \vartheta_2 \cos \varphi_2 \tag{11}$$

$$2 \sin(\tfrac{1}{2} \theta_{12}) \cos \Psi = \sin \vartheta_2 \cos(\varphi_2 - \Phi) - \sin \vartheta_1 \cos(\varphi_1 - \Phi) \tag{12}$$

$$2 \sin(\tfrac{1}{2} \theta_{12}) \sin \Psi = (\cos \vartheta_2 - \cos \vartheta_1) \sin \theta$$
$$- \sin \vartheta_1 \sin(\varphi_1 - \Phi) + \sin \vartheta_2 \sin(\varphi_2 - \Phi) \tag{13}$$

$$\cos \theta_{12} = \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_1 - \varphi_2) \tag{14}$$

The latter relation is, of course, the well known expansion for the angle between two vectors.

It is also of interest to give the vectors $\hat{\underline{r}}_1$ and $\hat{\underline{r}}_2$ in the particle plane: (primed co-ordinate system):

$$\hat{\underline{r}}_1 = \tilde{\underline{i}}' \sin(\Psi - \tfrac{1}{2} \theta_{12}) - \hat{\underline{j}}' \cos(\Psi - \tfrac{1}{2} \theta_{12}) \tag{15}$$

$$\hat{\underline{r}}_2 = \hat{\underline{i}}' \sin(\Psi + \tfrac{1}{2} \theta_{12}) - \hat{\underline{j}}' \cos(\Psi + \tfrac{1}{2} \theta_{12}) \tag{16}$$

$$\hat{\underline{z}} = \hat{\underline{j}}' \sin \theta + \hat{\underline{k}}' \cos \theta \tag{17}$$

$$\hat{y} = \hat{i}' \, \text{Sin} \, \Phi \; + \; \hat{j}' \, \text{Cos} \, \theta \, \text{Cos} \, \Phi \; - \; \hat{k}' \, \text{Sin} \, \theta \, \text{Cos} \, \Phi \tag{18}$$

$$\hat{x} = \hat{i}' \, \text{Cos} \, \Phi \; - \; \hat{j}' \, \text{Cos} \, \theta \, \text{Sin} \, \Phi \; + \; \hat{k}' \, \text{Sin} \, \theta \, \text{Sin} \, \Phi \tag{19}$$

The following relations which are also very useful can now simply be derived by computing $(\hat{r}_1 \cdot \hat{z})$ and $(\hat{r}_2 \cdot \hat{z})$ in the primed system.

$$\text{Cos} \, \theta_1 = - \, \text{Sin} \, \theta \, \text{Cos} (\Psi - \tfrac{1}{2} \theta_{12}) \tag{20a}$$

$$\text{Cos} \, \theta_2 = - \, \text{Sin} \, \theta \, \text{Cos} (\Psi + \tfrac{1}{2} \theta_{12}) \tag{20b}$$

$$\text{Sin} \, \theta_1 \, \text{Cos} \, \varphi_1 = \text{Cos} \, \Phi \, \text{Sin} \left(\Psi - \tfrac{1}{2} \theta_{12}\right) - \text{Cos} \, \theta \, \text{Sin} \, \Phi \, \text{Cos} \left(\Psi - \tfrac{1}{2} \theta_{12}\right) \tag{21a}$$

$$\text{Sin} \, \theta_2 \, \text{Cos} \, \varphi_2 = \text{Cos} \, \Phi \, \text{Sin} \left(\Psi + \tfrac{1}{2} \theta_{12}\right) - \text{Cos} \, \theta \, \text{Sin} \, \Phi \, \text{Cos} \left(\Psi + \tfrac{1}{2} \theta_{12}\right) \tag{21b}$$

$$\text{Sin} \, \theta_1 \, \text{Sin} \, \varphi_1 = \text{Sin} \, \Phi \, \text{Sin} \left(\Psi - \tfrac{1}{2} \theta_{12}\right) - \text{Cos} \, \theta \, \text{Cos} \, \Phi \, \text{Cos} (\Psi - \tfrac{1}{2} \theta_{12}) \tag{22a}$$

$$\text{Sin} \, \theta_2 \, \text{Sin} \, \varphi_2 = \text{Sin} \, \Phi \, \text{Sin} \left(\Psi + \tfrac{1}{2} \theta_{12}\right) - \text{Cos} \, \theta \, \text{Cos} \, \Phi \, \text{Cos} \left(\Psi + \tfrac{1}{2} \theta_{12}\right) \tag{22b}$$

III. PROPERTIES UNDER PARITY AND EXCHANGE

The operation of parity corresponds to the simultaneous inversion of both particles; coordinates: $r_1 \rightarrow -r_1$, $r_2 \rightarrow -r_2$. It can be seen from figure 1 that this places r_1 and r_2 facing the opposite direction, but the cross product and hence $\hat{z}'$ will not

change as a result of this operation. Thus the z-z' plane will
not change and $\hat{\underset{\sim}{x}}'$ will not change. On the other hand $(\hat{\underset{\sim}{r}}_2-\hat{\underset{\sim}{r}}_1)$
goes into the negative of itself, so that ψ gets increased by π .
In other words under <u>parity</u>

$$\theta \to \theta$$
$$\phi \to \phi$$
$$\psi \to \psi + \pi$$

(23)

Exchange corresponds to the transformation $\underset{\sim}{r}_1 \leftrightarrows \underset{\sim}{r}_2$. From the
analytical definitions $\hat{\underset{\sim}{z}}'$ and $\hat{\underset{\sim}{x}}'$, Eqs. (1) and (2), the new primed axes
will go into the negative of themselves. Also $(\hat{\underset{\sim}{r}}_2-\hat{\underset{\sim}{r}}_1)$ goes into
negative of itself. Clearly the inversion of the z' axis corres-
ponds to the transformation $\theta \to \pi - \theta$. Noting that ϕ is the
angle in the x-y plane and measured as positive with respect
to the z axis, which is fixed, we see that $\phi \to \pi + \phi$. The
simultaneous inversion of $\hat{\underset{\sim}{x}}'$ and $(\underset{\sim}{r}_2-\underset{\sim}{r}_1)$ means that the modulus
of the angle ψ remains the same. However, since ψ is an angle
in the x'-y' plane, it is measured as positive with respect to the
z' axis. Since the latter goes into the negative itself, it
becomes clear that $\psi \to 2\pi - \psi$. Thus we have under <u>exchange</u>

$$\theta \to \pi - \theta$$
$$\phi \to \phi + \pi$$
$$\psi \to 2\pi - \psi$$

(24)

The significance of these transformations relates to the transformation properties of the vector spherical harmonics under the same operation. These functions, which are the eigenfunctions of the angular momentum (next section), are the basic functions in terms of which the complete wave function is expanded. They can be written

$$\mathcal{D}_{\ell}^{m,k}(\theta,\phi,\psi) = \sqrt{\frac{2(2\ell+1)}{4\pi}} \; e^{i(m\phi+k\psi)} \; d_{\ell}^{m,k}(\theta) \tag{25}$$

where the normalization has been so chosen that the function is identical with what is given in section IV and the $d_{\ell}^{m,k}(\theta)$ agree with those given by Wigner[8]. Only the dependence on θ is non-trivial; for $m \geqslant k \geqslant 0$

$$d_{\ell}^{m,k}(\theta) = \sqrt{\frac{(\ell+m)!\,(\ell-k)!}{(\ell-m)!\,(\ell+k)!}} \; \cos^{2\ell+k-m}\tfrac{1}{2}\theta \; \cdot \; \sin^{m-k}\tfrac{1}{2}\theta$$

$$\cdot \; F(m-\ell,\,-k-\ell,\,m-k+1,\,-\tan^2\tfrac{1}{2}\theta) \tag{26}$$

$F(a,b;\,c;\,z)$ is the hypergeometric function in the notation of Magnus and Oberhettinger[9]. The important property of $d_{\ell}^{m,k}(\theta)$, proved in Wigner's book[8], is:

$$d_{\ell}^{m,k}(\pi-\theta) = (-1)^{\ell-m} \cdot d_{\ell}^{m,-k}(\theta) \tag{27}$$

Letting P and $\mathcal{E}_{12}$ represent parity and exchanges we have from (23) and (24):

$$P\,\mathcal{D}_{\ell}^{m,k}(\theta,\phi,\psi) = \mathcal{D}_{\ell}^{m,k}(\theta,\phi,\psi+\pi)$$

$$\mathcal{E}_{12}\,\mathcal{D}_{\ell}^{m,k}(\theta,\phi,\psi) = \mathcal{D}_{\ell}^{m,k}(\pi-\theta,\phi+\pi,2\pi-\psi)$$

which using (27) reduce to

$$P \, \mathcal{D}_\ell^{m,k}(\theta, \Phi, \Psi) = (-1)^k \, \mathcal{D}_\ell^{m,k}(\theta, \Phi, \Psi) \tag{28}$$

$$\mathcal{E}_{12} \, \mathcal{D}_\ell^{m,k}(\theta, \Phi, \Psi) = (-1)^\ell \, \mathcal{D}_\ell^{m,-k}(\theta, \Phi, \Psi) \tag{29}$$

The simplicity of Eq. (29) is the essential feature which recommends Holmberg's angles to the description of the two electron problem.

IV. ANGULAR MOMENTUM

The components of the total angular momentum are readily expressed in terms of the particles' spherical angles. Thus, for example

$$-\frac{i}{\hbar} M_x = \sin \varphi_1 \frac{\partial}{\partial \vartheta_1} + \cot \vartheta_1 \cos \varphi_1 \frac{\partial}{\partial \varphi_1} + \sin \varphi_2 \frac{\partial}{\partial \vartheta_2}$$
$$+ \cot \vartheta_2 \cos \varphi_2 \frac{\partial}{\partial \varphi_2} \tag{30}$$

The particles' angles ϑ_1, φ_1, ϑ_2, φ_2 via (9) - (14) are implicit functions of the four angles θ, Φ, Ψ, θ_{12}. Thus the problem of finding M_x in these angles is a straightforward problem of partial differentiation. We can write

$$-\frac{i}{\hbar} M_x = A_\theta \frac{\partial}{\partial \theta} + A_\Phi \frac{\partial}{\partial \Phi} + A_\Psi \frac{\partial}{\partial \Psi} + A_{\theta_{12}} \frac{\partial}{\partial \theta_{12}}$$

where

$$A_\chi = \sin \varphi_1 \frac{\partial \chi}{\partial \vartheta_1} + \sin \varphi_2 \frac{\partial \chi}{\partial \vartheta_2} + \cot \vartheta_1 \cos \varphi_1 \frac{\partial \chi}{\partial \varphi_1} + \cot \vartheta_2 \cos \varphi_2 \frac{\partial \chi}{\partial \varphi_2} \tag{31}$$

and χ can be anyone of the angles θ, Φ , Ψ , or θ_{12}. Using then Eqs. (9) - (14), one finds that the following relations fall out quite easily:

$$A_{\theta_{12}} = 0 \tag{32}$$

$$A_\theta = - \cos \Phi \tag{33}$$

$$A_\Phi = \sin \Phi \cos \theta \tag{34}$$

$$A_\Psi = - \frac{\sin \Phi}{\sin \theta} \tag{35}$$

Thus

$$M_\chi = \frac{\hbar}{i} \left[\cos \Phi \frac{\partial}{\partial \theta} - \sin \Phi \cos \theta \frac{\partial}{\partial \Phi} + \frac{\sin \Phi}{\sin \theta} \frac{\partial}{\partial \Psi} \right] . \tag{36}$$

One can, of course, proceed in a completely analogous way to get the remaining components of the angular momentum, however, let us note from Eqs. (20) that

$$\frac{\partial \vartheta_1}{\partial \Phi} = \frac{\partial \vartheta_2}{\partial \Phi} = 0 \tag{37}$$

and from (10) and (11)

$$\frac{\partial \varphi_1}{\partial \Phi} = \frac{\partial \varphi_2}{\partial \Phi} = 1 \tag{38}$$

Since

$$\frac{\partial}{\partial \phi} = \sum_{j=1}^{2} \left(\frac{\partial \varphi_j}{\partial \phi} \cdot \frac{\partial}{\partial \varphi_j} + \frac{\partial \vartheta_j}{\partial \phi} \cdot \frac{\partial}{\partial \vartheta_j} \right)$$

substitution of (37) and (38)   yields

$$\frac{\partial}{\partial \phi} = \frac{\partial}{\partial \varphi_1} + \frac{\partial}{\partial \varphi_2}$$

However, since

$$M_z = \frac{\hbar}{i} \left(\frac{\partial}{\partial \varphi_1} + \frac{\partial}{\partial \varphi_2} \right)$$

we therefore have the z-component of $\underset{\sim}{M}$:

$$M_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \tag{39}$$

The remaining component of the angular momentum may be derived from the commutation relation $\left[M_z , M_x \right] = i\hbar \, M_y$ Straightforward substitution yields:

$$M_y = \frac{\hbar}{i} \left[\text{Sin} \, \phi \, \frac{\partial}{\partial \theta} + \text{Cos} \, \phi \, \text{Cot} \, \theta \, \frac{\partial}{\partial \phi} - \frac{\text{Cos} \, \phi}{\text{Sin} \, \theta} \cdot \frac{\partial}{\partial \psi} \right] \tag{40}$$

These relations are independent of θ_{12} corresponding to the statement that the angular momentum only depends on the (three) Euler angles θ, ϕ, ψ. The forms of the three operators is the same as one gets with the Hylleraas-Breit angles[3]. The square of the angular momentum is likewise the same. One finds directly

from the sum of the squares that

$$M^2 = -\hbar^2 \left[(1 + \cot^2\theta) \frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\psi^2} \right.$$
$$\left. - 2 \frac{\cot\theta}{\sin\theta} \frac{\partial^2}{\partial\phi\partial\psi} + \cot\theta \frac{\partial}{\partial\theta} \right] \tag{41}$$

The vector spherical harmonics, which have been given for the restricted range $m \gtrless k \geqslant 0$ in Eq. (25), are the similtaneous eigenfunctions of $\underset{\sim}{M}^2$ with eigenvalue $\hbar^2 \ell(\ell+1)$ and $\hbar m$

$$\underset{\sim}{M}^2 \, \mathcal{D}_\ell^{m,k}(\theta, \phi, \psi) = \hbar^2 \ell(\ell+1) \mathcal{D}_\ell^{m,k}(\theta, \phi, \psi) \tag{42}$$

$$M_z \, \mathcal{D}_\ell^{m,k}(\theta, \phi \, \psi) = \hbar m \cdot \mathcal{D}_\ell^{m,k}(\theta, \phi, \psi) \tag{43}$$

They are given in a completely general, normalized form in Pauling and Wilson[10]:

$$\mathcal{D}_\ell^{m,k}(\theta, \phi, \psi) = N_{\ell m k} \sin^{|k-m|}\tfrac{1}{2}\theta \, \cos^{|k+m|}\tfrac{1}{2}\theta \, e^{i(m\phi + k\psi)}$$
$$\times F(-\ell + \tfrac{1}{2}\beta - 1, \ell + \tfrac{1}{2}\beta, 1 + |k-m|, \sin^2\tfrac{\theta}{2}) \tag{44}$$

where

$$\beta = |k+m| + |k-m| + 2 \tag{45}$$

and the normalization constant is

$$N_{\ell m k} = \left[\frac{(2\ell+1)(\ell + \tfrac{1}{2}|k+m| + \tfrac{1}{2}|k-m|)! (\ell - \tfrac{1}{2}|k+m| + \tfrac{1}{2}|k-m|)!}{8\pi^2(\ell - \tfrac{1}{2}|k+m| - \tfrac{1}{2}|k-m|)! (\ell + \tfrac{1}{2}|k+m| - \tfrac{1}{2}|k-m|)! (|k-m|!)^2} \right]^{\frac{1}{2}} \tag{46}$$

In addition to the usual magnetic quantum number m, the vector spherical harmonics depend on the quantum number k, an integer whose range of values is the same as m: $-\ell \leqslant$ m, k $\leqslant \ell$. The physical significance of k derives from the fact that the $\mathcal{Y}_\ell^{m,k}$ are the eigenfunctions of the spherical top (for which (42) is the Schrödinger equation), and k is the angular momentum quantum number about the body-fixed axis of rotation. With regard to the applications that we contemplate here, k can be considered a degeneracy label which must be adjusted such that other requirements are fulfilled.

V.   CONSTRUCTION OF THE TOTAL WAVE FUNCTION

We shall confine ourselves here strictly to the atomic problem which implies that the potential energy as well as the kinetic energy commutes with the total angular momentum. In this case the total wave function for a given ℓ must be a linear superposition of the degenerate $\mathcal{Y}_\ell^{m,k}$. In addition, m will be fixed for a given magnetic substate and the "radial" equations will be independent of m (cf. Appendix II).

Considering, for the moment, the residual coordinates as r_1, r_2, θ_{12}, we can therefore expand the total wave function in the form:

$$\Psi_{\ell m}(\underline{r}_1 \cdot \underline{r}_2) = \sum_{k=-\ell}^{\ell} \mathfrak{z}_\ell^k(r_1, r_2, \theta_{12}) \, \mathcal{Y}_\ell^{m,k}(\theta, \Phi, \psi)$$

$$(47)$$

The parity operations, Eq. (23), only effects the Euler angles, and from Eq. (28) it only multiplies the $\mathcal{D}_\ell^{m,\nu}$ function by $(-1)^k$. Therefore by restricting the sum to even and odd values of k, we guarantee that the superpositions have even and odd parity respectively:

$$\Psi_{\ell m}^{even}(\underline{r}_1 , \underline{r}_2) = \sum_{k\ even}^{''} g_\ell^k(r_1, r_2, \theta_{12})\ \mathcal{D}_\ell^{m,K}(\theta. \Phi, \Psi) \tag{48a}$$

$$\Psi_{\ell m}^{odd}(\underline{r}_1, \underline{r}_2) = \sum_{k\ odd}^{''} g_\ell^k(r_1, r_2, \theta_{12})\ \mathcal{D}_\ell^{m,K}(\theta, \Phi, \Psi). \tag{48b}$$

where the double prime on the summation emphasizes that the sum goes over every other value of k.

In deriving the radial equations (next section) we shall exploit the invariance of the radial equations with respect to m, by choosing m = 0. When the Hamiltonian is written in terms of the Euler angles and the remaining variables, there will occur terms

involving $\frac{\partial}{\partial \Phi}$ and $\frac{\partial}{\partial \Psi}$. By virtue of m = 0, the former terms vanish, but the latter terms would bring down the imaginary coefficient ik. In order to avoid complex equations, it is therefore convenient to construct real angular momentum functions. Let

$$\mathcal{D}_\ell^{X+} = \frac{1}{\sqrt{2}}(\mathcal{D}_\ell^{0,X} + \mathcal{D}_\ell^{0,-X}) = \frac{\sqrt{2\ell+1}}{2\pi}\ \cos X\Psi\ d_\ell^{0,X}(\theta) \tag{49a}$$

$$\mathcal{D}_\ell^{X-} = \frac{1}{\sqrt{2}\,i}(\mathcal{D}_\ell^{0,X} - \mathcal{D}_\ell^{0,-X}) = \frac{\sqrt{2\ell+1}}{2\pi}\cdot \sin X\Psi\ d_\ell^{0,X}(\theta) \tag{49b}$$

for $\varkappa > 0$, where

$$\varkappa = |k| \tag{50}$$

and for $\varkappa = 0$ define

$$\mathcal{D}_\ell^{0+} \equiv \mathcal{D}_\ell^{0,0} \quad , \quad \mathcal{D}_\ell^{0-} = 0 \tag{49c}$$

This then constitutes a set of real, orthonormal vector spherical harmonics (note $d_\ell^{0;\varkappa} = d_\ell^{0,-k}$). These real vector spherical harmonics are still eigenfunctions of parity with eigenvalue $(-1)^\varkappa$.

The property of exchange is a mite more complicated than parity in the sense that it affects not only the Euler angles, but the residual coordinates as well. The beauty and importance of Holmber's angles, however, is that there is no mixing, and independent of whether we consider the residual variables r_1, r_2, θ_{12} or r_1, r_2, r_{12}, the effect of exchange on the residual coordinates is simply $r_1 \rightleftarrows r_2$.

Finally then, if we construct

$$\Psi_{\ell 0}(\mathbf{r}_1, \mathbf{r}_2) = \sum_\varkappa \left[f_\ell^{\varkappa+}(r_1, r_2, \theta_{12}) \cdot \mathcal{D}_\ell^{\varkappa+}(\theta, \phi, \psi) \right. $$
$$\left. + f_\ell^{\varkappa-}(r_1, r_2, \theta_{12}) \, \mathcal{D}_\ell^{\varkappa-}(\theta, \phi, \psi) \right] , \tag{51}$$

the operation of exchange on this sum then gives, with the use of (29), :

$$\mathcal{E}_{12} \, \Psi_{lo} (\underset{\sim}{r_1}, \underset{\sim}{r_2}) = \Psi_{lo} (\underset{\sim}{r_2}, \underset{\sim}{r_1})$$

$$= \sum_{\mathcal{X}}^{n} \left[f_l^{\mathcal{X}+}(\underset{\sim}{r_2}, \underset{\sim}{r_1}, \theta_{12}) \, (-1)^l \, \mathcal{D}_l^{\mathcal{X}+}(\theta, \Phi, \Psi) \right.$$

$$\left. + f_l^{\mathcal{X}-}(\underset{\sim}{r_2}, \underset{\sim}{r_1}, \theta_{12}) \, (-1)^{l+1} \, \mathcal{D}_l^{\mathcal{X}-}(\theta, \Phi, \Psi) \right]$$

Thus if

$$f_l^{\mathcal{X}+}(r_2, r_1, \theta_{12}) = \pm (-1)^l \cdot f_l^{\mathcal{X}+}(r_1, r_2, \theta_{12}) \qquad (52a)$$

$$f_l^{\mathcal{X}-}(r_2, r_1, \theta_{12}) = \pm (-1)^{l+1} \cdot f_l^{\mathcal{X}-}(r_1, r_2, \theta_{12}), \qquad (52b)$$

the function Ψ_{lo} of Eq. (51) is a real, space symmetric (upper sign) or space antisymmetric (lower sign), eigenfunction of $\underset{\sim}{M^2}$ and M_z corresponding to the quantum numbers l and m with m = 0. The space symmetric and antisymmetric solutions correspond to singlet and triplet spin states respectively. Furthermore the restriction to m = 0 is sufficient for deriving the radial equations.

We have shown that the m = 0 function can be written in manifestly real form, Eq. (51). However in that form, it is not obvious what the generalization is to arbitrary m states. The generalization is nevertheless simply obtained. Let

$$g_l^{\mathcal{X}} = \frac{1}{\sqrt{2}} \left(f_l^{\mathcal{X}+} - i \, f_l^{\mathcal{X}-} \right) \qquad (53)$$

$$\mathcal{X} > 0$$

and

$$q_\ell^{-\varkappa} = \frac{1}{\sqrt{2}} \left(f_\ell^{\varkappa +} + i\, f_\ell^{\varkappa -} \right)$$

then the form (51) reduces to that of Eq. (47) for m = 0. For arbitrary m one then need only replace the $\mathcal{D}_\ell^{0,\varkappa}$ functions by the appropriate $\mathcal{D}_\ell^{m,\varkappa}$ functions, the radial q_ℓ^k functions remaining the same.

Alternatively one can define generalizations of the $\mathcal{D}_\ell^{\varkappa \pm}$, Eq. (49), for arbitrary m.

$$\mathcal{D}_\ell^{m,\varkappa +} \equiv \frac{1}{\sqrt{2}} \left(\mathcal{D}_\ell^{m,\varkappa} + \mathcal{D}_\ell^{m,-\varkappa} \right) \qquad \varkappa > 0 \; , \; m \neq 0 \tag{54a}$$

$$\mathcal{D}_\ell^{m,\varkappa -} \equiv \frac{1}{\sqrt{2}\,i} \left(\mathcal{D}_\ell^{m,\varkappa} - \mathcal{D}_\ell^{m,-\varkappa} \right)$$

with $\quad \mathcal{D}_\ell^{(0,\varkappa)\pm} \equiv \mathcal{D}_\ell^{\varkappa \pm} \qquad$ for m = 0. For $\varkappa = 0$

$$\mathcal{D}_\ell^{(m,0)+} \equiv \mathcal{D}_\ell^{m,0} \quad , \quad \mathcal{D}_\ell^{(m,0)-} = 0 \tag{54b}$$

The complete function for arbitrary m can then be written

$$\Psi_{\ell m}(\underset{\sim}{r_1}, \underset{\sim}{r_2}) = \sum_\varkappa{}'' \left[f_\ell^{\varkappa +} \mathcal{D}_\ell^{m,\varkappa +} + f_\ell^{\varkappa -} \mathcal{D}_\ell^{m,\varkappa -} \right] \tag{55}$$

In this case the "radial" functions $f_\ell^{\varkappa \pm}$ are the same as in (51), hence real; whereas the angular functions become altered. Note for m ≠ 0, however, that the modified spherical harmonics, $\mathcal{D}_\ell^{(m,\varkappa)\pm}$ are no longer real.

VI. THE KINETIC ENERGY

Just as in the case of the angular momentum, the kinetic energy can be obtained by a straightforward process of partial differentiation.

In this case, however, since second partial derivatives are involved, the differentiation is a much longer job, and, as we shall see, the partial derivatives involving θ_{12} no longer cancel out.

We start then with the kinetic energy in spherical coordinates

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1}\frac{\partial^2}{\partial r_1}r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2}r_2 + \frac{1}{r_1^2}\left[\frac{1}{\sin\vartheta_1}\frac{\partial}{\partial\vartheta_1}\sin\vartheta_1\frac{\partial}{\partial\vartheta_1} + \frac{1}{\sin^2\vartheta_1}\frac{\partial^2}{\partial\varphi_1^2}\right]$$
$$+ \frac{1}{r_2}\left[\frac{1}{\sin\vartheta_2}\frac{\partial}{\partial\vartheta_2}\sin\vartheta_2\frac{\partial}{\partial\vartheta_2} + \frac{1}{\sin^2\vartheta_2}\frac{\partial^2}{\partial\varphi_2^2}\right] \tag{56}$$

The first two terms are, of course, unaffected by the transformation. The angular differentiations then involve the transformation from the variables θ_1, φ_1, θ_2, φ_2 to θ, ϕ, ψ, and θ_{12}.

Consider the coefficient of the r_1^{-2} term. After some regrouping, we can write

$$\frac{1}{\sin\vartheta_1}\frac{\partial}{\partial\vartheta_1}\sin\vartheta_1\frac{\partial}{\partial\vartheta_1} + \frac{1}{\sin^2\vartheta_1}\cdot\frac{\partial^2}{\partial\varphi_1^2} = \sum_{\alpha=1}^{4}\left[\left(\frac{\partial\chi_\alpha}{\partial\vartheta_1}\right)^2 + \frac{1}{\sin^2\vartheta_1}\left(\frac{\partial\chi_\alpha}{\partial\varphi_1}\right)^2\right]\frac{\partial^2}{\partial\chi_\alpha^2}$$
$$+ \sum_{\alpha}\left[\frac{\partial^2\chi_\alpha}{\partial\vartheta_1^2} + \frac{1}{\sin^2\vartheta_1}\frac{\partial^2\chi_\alpha}{\partial\varphi_1^2} + \cot\vartheta_1\frac{\partial\chi_\alpha}{\partial\vartheta_1}\right]\frac{\partial}{\partial\chi_\alpha}$$
$$+ 2\sum_{\alpha>\beta=1}\sum\left[\frac{\partial\chi_\alpha}{\partial\vartheta_1}\frac{\partial\chi_\beta}{\partial\vartheta_1} + \frac{1}{\sin^2\vartheta_1}\frac{\partial\chi_\alpha}{\partial\varphi_1}\frac{\partial\chi_\beta}{\partial\varphi_1}\right]\frac{\partial^2}{\partial\chi_\alpha\partial\chi_\beta} \tag{57}$$

where for $\alpha = 1, 2, 3, 4$, χ_α refers to θ, ϕ, ψ, θ_{12}. The problem thus reduces to finding each of the square brackets separately in terms of the Euler angles and θ_{12}. The results are given in Table I.

The kinetic energy thus becomes

$$\nabla_1^2 + \nabla_2^2 = \left\{\frac{1}{r_1}\frac{\partial^2}{\partial r_1}r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2}r_2 + \right.$$
$$\left.\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right\} + \frac{F_1}{r_1^2} + \frac{F_2}{r_2^2} \tag{58}$$

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where

$$F_1 = \frac{1}{\sin^2\theta_{12}}\left[\sin^2(\psi+\tfrac{\theta_{12}}{2})\frac{\partial^2}{\partial\theta^2} + \cos^2(\psi+\tfrac{\theta_{12}}{2})\cot\theta\frac{\partial}{\partial\theta} \right.$$

$$+ \cos^2(\psi+\tfrac{\theta_{12}}{2})\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \sin(2\psi+\theta_{12})\frac{\cot\theta}{\sin\theta}\frac{\partial}{\partial\phi}$$

$$- \sin(2\psi+\theta_{12})\frac{1}{\sin\theta}\frac{\partial^2}{\partial\theta\partial\phi} + \sin(2\psi+\theta_{12})\cot\theta\frac{\partial^2}{\partial\psi\partial\theta}$$

$$\left. - 2\cos^2(\psi+\tfrac{\theta_{12}}{2})\frac{\cot\theta}{\sin\theta}\frac{\partial^2}{\partial\psi\partial\phi} \right] - \frac{\partial^2}{\partial\psi\partial\theta_{12}} + A_1\frac{\partial^2}{\partial\psi^2} + B_1\frac{\partial}{\partial\psi} \tag{59}$$

and

$$A_1 = \frac{1}{4} + \frac{\cot^2\theta}{\sin^2\theta_{12}}\cos^2(\psi+\tfrac{\theta_{12}}{2}) \tag{60}$$

$$B_1 = -\frac{\cos\psi\,\sin(\psi+\theta_{12})}{\sin^2\theta_{12}} - \frac{\cot^2\theta\,\sin(2\psi+\theta_{12})}{\sin^2\theta_{12}}$$

$$+ \frac{\cos\theta_{12}}{2\sin\frac{\theta_{12}}{2}}\left(1-\frac{1}{\cos\frac{\theta_{12}}{2}}\right) \tag{61}$$

The expressions for F_2, A_2 and B_2 can be obtained by replacing θ_{12} by $-\theta_{12}$ in the above formulae (including the appropriate partial derivatives):

$$F_2(\theta, \phi, \psi, \theta_{12}) = F_1(\theta, \phi, \psi, -\theta_{12}) \tag{62}$$

It is clear, since all the coefficients are independent of ϕ, that M_z commutes with the kinetic energy. We have also explicitly

verified that $\left[M_x, \nabla_1{}^2 + \nabla_2{}^2\right] = 0.$

Note that the partial derivative involving θ_{12} and no other angles has been placed in the curly brackets with the radial derivatives. This is because this term, as the radial derivatives themselves, do not affect the orbital angular momentum, and are the only terms which act on total S states[1,2,3].

In fact, in the action of the remaining terms on the angular momentum eigenfunction rests the bulk of the reduction of the Schrödinger equation to its 3-dimensional "radial" form. With this reduction in mind (cf. next section), it is convenient to write F_1 in terms of operators whose effect on the angular momentum eigenfunctions is particularly simple. One can show

$$F_1 = \frac{1}{2}\sin{}^2\theta_{12}\left[-\frac{1}{\hbar^2}M^2 + \cos\theta_{12}(\sin 2\psi\, \Lambda_2 - \cos 2\psi\, \Lambda_1)\right.$$

$$\left. + \sin\theta_{12}(\sin 2\psi\, \Lambda_1 + \cos 2\psi\, \Lambda_2)\right]$$

$$- \frac{\partial^2}{\partial\theta_{12}\partial\psi} + \left(\frac{1}{4} - \frac{1}{2}\frac{1}{\sin{}^2\theta_{12}}\right)\frac{\partial^2}{\partial\psi^2} \tag{63}$$

$$+ \left(\frac{\cos\theta_{12}}{2\sin\theta_{12}} - \cot\theta_{12} - \frac{1}{2\sin\theta_{12}}\right)\frac{\partial}{\partial\psi}$$

where

$$\Lambda_1 = 2\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2}{\partial\psi^2} + \frac{1}{\hbar^2}M^2$$

$$\tag{64}$$

$$\Lambda_2 = 2\frac{\cot\theta}{\sin\theta}\frac{\partial}{\partial\phi} - \frac{2}{\sin\theta}\frac{\partial^2}{\partial\theta\partial\phi} + 2\cot\theta\frac{\partial^2}{\partial\psi\partial\theta}$$

$$- \left(1 + 2\cot{}^2\theta\right)\frac{\partial}{\partial\psi}$$

and $\underline{M}^2$ is the total angular momentum squared operator given in
Eq. (41). F_2 is again derivable from F_1 by replacing θ_{12} by $-\theta_{12}$.

VII. THE REDUCED OR RADIAL EQUATIONS, ATOMIC CASE

The essential properties of the combinations of the operators
appearing in F_1 and F_2, Eq. (62), are the following (cf. Appendix I):

$$
(\operatorname{Sin}2\psi\,\Lambda_2 - \operatorname{Cos}2\psi\,\Lambda_1)\,\mathcal{J}_\ell^{\chi+} = -2\chi(\chi-1)\,\beta_{\ell\chi}\,(1-\delta_{0,\chi})\,\mathcal{J}_\ell^{(\chi-2)+} + \delta_{1,\chi}(1-2A_\chi^\ell)\,\mathcal{J}_\ell^{\chi+}
$$

$$
- \frac{(1+3\delta_{0,\chi})}{[1+\delta_{0,\kappa}(\sqrt{2}-1)]}\cdot A_\chi^\ell\,A_{\chi+1}^\ell\,\frac{1}{2\beta_{\ell,\chi+2}}\,\mathcal{J}_\ell^{(\chi+2)+} \tag{65a}
$$

$$
(\operatorname{Sin}2\psi\,\Lambda_1 + \operatorname{Cos}2\psi\,\Lambda_2)\,\mathcal{J}_\ell^{\chi+} = -2\chi(\chi-1)\,\beta_{\ell\chi}(1-\delta_{3,\chi})(1-\delta_{0,\chi})\,\mathcal{J}_\ell^{(\chi-2)-}
$$

$$
- \delta_{1,\chi}(1-2A_\chi^\ell)\,\mathcal{J}_\ell^{\chi-} + \frac{(1+3\delta_{0,\chi})}{[1+\delta_{0,\chi}(\sqrt{2}-1)]}\,A_\chi^\ell\,A_{\chi+1}^\ell\,\frac{1}{2\beta_{\ell,\chi+2}}\,\mathcal{J}_\ell^{(\chi+2)-} \tag{65b}
$$

$$
(\operatorname{Sin}2\psi\,\Lambda_2 - \operatorname{Cos}2\psi\,\Lambda_1)\,\mathcal{J}_\ell^{\chi-} = -2\chi(\chi-1)\,\beta_{\ell\chi}\,(1-\delta_{3\chi})(1-\delta_{0,\chi})\,\mathcal{J}_\ell^{(\chi-2)-}
$$

$$
- \delta_{1,\chi}(1-2A_\chi^\ell)\,\mathcal{J}_\ell^{\chi-} - \frac{(1-\delta_{0,\chi})}{[1+\delta_{0,\chi}(\sqrt{2}-1)]}\,A_\chi^\ell\,A_{\chi+1}^\ell\,\frac{1}{2\beta_{\ell\chi+2}}\,\mathcal{J}_\ell^{(\chi+2)-} \tag{66a}
$$

$$
(\operatorname{Sin}2\psi\,\Lambda_1 + \operatorname{Cos}2\psi\,\Lambda_2)\,\mathcal{J}_\ell^{\chi-} = 2\chi(\chi-1)\,\beta_{\ell\chi}\,(1-\delta_{0,\chi})\,\mathcal{J}_\ell^{(\chi-2)+}
$$

$$
- \delta_{1,\chi}(1-2A_\chi^\ell)\,\mathcal{J}_\ell^{\chi+} - \frac{(1-\delta_{0,\chi})}{1+\delta_{0,\chi}(\sqrt{2}-1)}\,A_\chi^\ell\,A_{\chi+1}^\ell\,\frac{1}{2\beta_{\ell,\chi+2}}\,\mathcal{J}_\ell^{(\chi+2)+} \tag{66b}
$$

where

$$A_x^\ell = \frac{(x - c)(x + \ell + 1)}{2(x+1)} \tag{67}$$

and

$$B_{\ell x} = \frac{[(\ell - x + 1)(\ell - x + 2)(\ell + x)(\ell + x - 1)]^{\frac{1}{2}}}{4x(x-1)} \tag{68}$$

Recall that x is the absolute value of k, Eq. (50). We have explicitly verified that these relationships are not altered if one replaces the $\mathcal{Y}_\ell^{x\pm}$ functions by the $\mathcal{Y}_\ell^{(m,x)\pm}$ functions of Eq. (54).(cf.Appendix II) This is, of course, necessary for the radial equations to be independent of m. With these relationships, it becomes quite simple to derive the reduced equations from the original Schrödinger equation

$$H \Psi_{\ell o} = E \Psi_{\ell o} \quad , \tag{69}$$

where the wave function $\Psi_{\ell o}$ is expanded in Eq. (51). One obtains

$$\left[L_{\theta_{12}} + \frac{2m}{\hbar^2}(E - V) \right] f_\ell^{x+} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left[\left\{ \frac{\ell(\ell+1) - x^2}{2 \sin \theta_{12}} + \frac{x^2}{4} - \frac{\cot \theta_{12}}{\sin \theta_{12}} \delta_{1,x} \right. \right.$$

$$\left. \cdot (1 - 2A_x^\ell) \right\} f_\ell^{x+}$$

$$+ \frac{\cot \theta_{12}}{\sin \theta_{12}} (x+1)(x+2) B_{\ell x+2} f_\ell^{(x+2)+} + \frac{\cot \theta_{12}}{4 \sin \theta_{12}} \frac{1 + 3\delta_{0,x-2}}{[1 + \delta_{0,x-2}(\sqrt{2}-1)]} \frac{A_{x-2}^\ell A_{x-1}^\ell}{B_{\ell x}} f_\ell^{(x-2)\pm} \right]$$

$$+ \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \left[x \left(\frac{\cos \theta_{12}}{2 \sin \frac{\theta_{12}}{2}} - \cot \theta_{12} - \frac{1}{2 \sin \theta_{12}} \right) f_\ell^{x-} - x \frac{\partial f_\ell^{x-}}{\partial \theta_{12}} \right.$$

$$- \delta_{1,x} \frac{(1 - 2A_x^\ell)}{2 \sin \theta_{12}} f_\ell^{x-} + \frac{(x+1)(x+2)}{\sin \theta_{12}} B_{\ell x+2} f_\ell^{(x+2)-}$$

$$\left. - \frac{1}{4 \sin \theta_{12}} \cdot \frac{1 - \delta_{0,x-2}}{1 + \delta_{0,x-2}(\sqrt{2}-1)} \frac{A_{x-2}^\ell A_{x-1}^\ell}{B_{\ell x}} f_\ell^{(x-2)-} \right] = 0 \tag{70a}$$

$$\left[L_{\theta_{12}} + 2\frac{m}{\hbar^2}(E-V) \right] f_\ell^{\varkappa -} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \Bigg[\left\{ \frac{\ell(\ell+1) - \varkappa^2}{2\sin^2\theta_{12}} + \frac{\varkappa^2}{4} \right.$$

$$+ \frac{\cot\theta_{12}}{2\sin\theta_{12}} \delta_{1,\varkappa}(1 - 2A_\varkappa^\ell) \Bigg\} f_\ell^{\varkappa -} + \frac{\cot\theta_{12}}{\sin\theta_{12}}(1 - \delta_{2,\varkappa+2})(\varkappa+1)(\varkappa+2)B_{\ell,\varkappa+2} f_\ell^{(\varkappa+2)}$$

$$+ \frac{\cot\theta_{12}}{4\sin\theta_{12}} \frac{(1 - \delta_{0,\varkappa-2}) A_{\varkappa-2}^\ell A_{\varkappa-1}^\ell}{[1 + \delta_{0,\varkappa-2}(\sqrt{2}-1)] B_{\ell\varkappa}} f_\ell^{(\varkappa-2)-} \Bigg] -$$

$$\left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \Bigg[-\varkappa \frac{\partial f^{\varkappa-}}{\partial\theta_{12}} + \varkappa \left(\frac{\cos\theta_{12}}{2\sin\theta_{12}} - \cot\theta_{12} - \frac{1}{2\sin\theta_{12}} \right) f_\ell^{\varkappa+}$$

$$+ \delta_{1,\varkappa}\frac{(1 - 2A_\varkappa^\ell)}{2\sin\theta_{12}} f_\ell^{\varkappa+} + (1 - \delta_{2,\varkappa+2})\frac{(\varkappa+1)(\varkappa+2)}{\sin\theta_{12}} B_{\ell,\varkappa+2} f_\ell^{(\varkappa+2)+}$$

$$- \frac{1 + 3\delta_{0,\varkappa-2}}{4\sin\theta_{12}} \cdot \frac{A_{\varkappa-2}^\ell \cdot A_{\varkappa-1}^\ell}{[1 + \delta_{0,\varkappa-2}(\sqrt{2}-1)]} \frac{1}{B_{\ell\varkappa}} f_\ell^{(\varkappa-2)+} \Bigg] = 0 \qquad (70b)$$

$L_{\theta_{12}}$ is the S wave part of the kinetic energy, and only the term containing it survives in the description of S states:[1,2,3]

$$L_{\theta_{12}} = \frac{1}{r_1}\frac{\partial^2 r_1}{\partial r_1} + \frac{1}{r_2}\frac{\partial^2 r_2}{\partial r_2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin\theta_{12}} \frac{\partial}{\partial\theta_{12}}\left(\sin\theta_{12} \frac{\partial}{\partial\theta_{12}} \right) \qquad (71)$$

Eq. (70) are the "radial" equations, which it has been our purpose to derive. They pertain to both types of parity and exchange states. Parity is determined by the evenness or oddness of $\varkappa$. If, for example, ℓ is even, and we want to describe a state of even parity, Eqs. (70) couple the functions $f_\ell^{\varkappa+}$ and $f_\ell^{\varkappa-}$ for $\varkappa = 0, 2, 4 \cdots \ell$. This involves $\ell/2$ pairs plus one function (for $\varkappa = 0$, $\mathcal{D}_\ell^{0-}$ is zero hence f_ℓ^{0-} can be taken to be zero) or $\ell + 1$ functions. The odd parity equations for the same ℓ correspond to the coupling of the function with $\varkappa = 1, 3, \ldots,$

$\ell - 1$. This relates $\ell/2$ pairs or ℓ functions to each other. Both even and odd parity together therefore involve $(2\ell + 1)$ functions corresponding the $(2\ell + 1)$ degeneracy of the vector spherical harmonics for a given m. For ℓ odd, there are ℓ functions involved in the even parity equations and $\ell + 1$ functions in the odd parity equations.

For a given parity and ℓ , both singlet and triplet (space symmetric and antisymmetric) states are described by the same set of equations. The differences in the solutions devolve from the different boundary conditions which must be applied, Eqs. (52). One of the key virtues of the functions $f_\ell^{\varkappa\pm}(r_1, r_2, \theta_{12})$ is that they are either symmetric or antisymmetric; thus they may be confined to the region, say $r_1 \not{/} r_2$. If, for example, ℓ is even so that the exchange character of $f_\ell^{\varkappa+}$ is symmetric (which, according to

(52), implies that $f_\ell^{\chi-}$ is antisymmetric), then these properties may be embodied in the boundary conditions[11]:

$$\left[\frac{\partial}{\partial n} f_\ell^{\chi+}(r_1, r_2, \theta_{12}) \right]_{r_1 = r_2} = 0 , \qquad (72)$$

where $\frac{\partial}{\partial n}$ represents the normal derivative, and

$$\left[f_\ell^{\chi-}(r_1, r_2, \theta_{12}) \right]_{r_1 = r_2} = 0 , \qquad (73)$$

and the solution from there on involves only the region $r_1 > r_2 > 0$. Such equations have distinct advantages from the point of view of numerical solutions[12].

One can define, however, an asymmetric function in terms of which the radial equations can be more simply written. Letting

$$F_\ell^\chi (r_1, r_2, \theta_{12}) \equiv f_\ell^{\chi+}(r_1, r_2, \theta_{12}) + f_\ell^{\chi-}(r_1, r_2, \theta_{12}) \qquad (74)$$

and

$$\widetilde{F}_\ell^\chi (r_1, r_2, \theta_{12}) \equiv f_\ell^{\chi+}(r_1, r_2, \theta_{12}) - f_\ell^{\chi-}(r_1, r_2, \theta_{12}) \qquad (75)$$

so that, from Eq. (47),

$$\widetilde{F}_\ell^\chi (r_2, r_1, \theta_{12}) = \pm (-1)^\ell F_\ell^\chi (r_1, r_2, \theta_{12}) \qquad (76)$$

one obtains by adding (70a) and (70b):

$$\left[L_{\theta_{12}} + \frac{2m}{\hbar^2}(E-V) \right] F_\ell^\varkappa - \left(\frac{1}{\gamma_1^2} + \frac{1}{\gamma_2^2} \right) \left[\left(\frac{\ell(\ell+1) - \varkappa^2}{2\sin^2\theta_{12}} + \frac{\varkappa^2}{4} \right) F_\ell^\varkappa \right.$$

$$- \delta_{1,\varkappa} \frac{\cot\theta_{12}}{2\sin\theta_{12}} (1 - 2A_\varkappa^\ell) \tilde{F}_\ell^\varkappa + (\varkappa+1)(\varkappa+2) \frac{\cot\theta_{12}}{\sin\theta_{12}} \beta_{\ell\varkappa+2} \left\{ F_\ell^{\varkappa+2} - S_{2,\varkappa+2}(\frac{F^{\varkappa+2} - \tilde{F}^{\varkappa+2}}{2}) \right.$$

$$+ \frac{\cot\theta_{12}}{4\sin\theta_{12}} \frac{A_{\varkappa-1}^\ell \cdot A_{\varkappa-1}^\ell}{\beta_{\ell\varkappa}\left[1 + \delta_{0,\varkappa-2}(\sqrt{2}-1)\right]} \right\} F_\ell^{\varkappa-2} + \delta_{0,\varkappa-2}(2\tilde{F}_\ell^{\varkappa-2} + F_\ell^{\varkappa-2}) \right\} \right] \qquad (77)$$

$$+ \left(\frac{1}{\gamma_1^2} - \frac{1}{\gamma_2^2} \right) \left[\varkappa \frac{\partial \tilde{F}_\ell^\varkappa}{\partial\theta_{12}} - \varkappa \left(\frac{\cos\theta_{12}}{2\sin\frac{\theta_{12}}{2}} - \cot\theta_{12} - \frac{1}{2\sin\theta_{12}} \right) \tilde{F}_\ell^\varkappa - \frac{\delta_{1,\varkappa}(1-2A_\varkappa^\ell) F_\ell^\varkappa}{2\sin\theta_{12}} \right.$$

$$+ \frac{(\varkappa+1)(\varkappa+2)}{\sin\theta_2} \beta_{\ell\varkappa+2} \left\{ -\tilde{F}_\ell^{\varkappa+2} + \frac{S_{2,\varkappa+2}}{2}(F_\ell^{\varkappa+2} + \tilde{F}_\ell^{\varkappa+2}) \right\} + \frac{A_{\varkappa-1}^\ell A_{\varkappa-1}^\ell \left\{ \tilde{F}_\ell^{\varkappa-2} + \delta_{0,\varkappa-2}(2F_\ell^{\varkappa-2} + \tilde{F}_\ell^{\varkappa-2}) \right\}}{\beta_{\ell\varkappa} 4\sin\theta_{12}\left[1 + \delta_{0,\varkappa-2}(\sqrt{2}-1)\right]} \right]$$

These equations, depending as they do on F_ℓ and $\tilde{F}_\ell$, are more analogous to the form the P-wave equation of Breit.[2] The question may arise in connection with these as well as Breit's equations, of whether they are well-defined, since they involve two functions $F_\ell^\varkappa$ and $\tilde{F}_\ell^\varkappa$ and yet there is only one equation (for a given $\varkappa$). This question, in fact would appear to be particularly relevant as the previous form of our equations,(70) do constitute a coupled set for a given $\varkappa$. To see that both situations are meaningful and in particular that (77) is well-defined, consider a numerical solution of (77). In that case the space of the independent variables is divided into a grid of points, and $F_\ell^\varkappa$ is the collection of numbers associated with these

grid points. F_ℓ^χ can therefore be considered a vector with as many components as there are grid points. The differential equation is replaced by a matrix which operates on the vector F_ℓ^χ . Now everytime an $\tilde{F}_\ell^\chi$ occurs in the equation, it is completely clear what has to be done: namely one must let the matrix counterpart of its coefficient in the differential equation operate on that component of F_ℓ^χ which is its reflection point defined by (76). This is a completely unambiguous prescription which is tantamount to saying that the set (77) is well defined by itself. The reason that (70) is composed of two equations for each χ whereas (77) is not is due to the fact that the functions F_ℓ^χ are asymmetric and therefore must be solved for in the whole r_1, r_2, θ_{12} space. On the other hand the $f_\ell^{\chi\pm}$ functions are either symmetric or anitsymmetric, and therefore they are restricted to the $r_1 \gtrless r_2$, θ_{12} (or equivalently to the $r_1 \leqslant r_2$, θ_{12}) space. Since this is only half the independent variable space, it is necessary that there be double the number of functions to recover the same information. This is again to say that (70) and (77) are completely equivalent. (Nevertheless a redundant equation with F_ℓ^χ and $\tilde{F}_\ell^\chi$ interchanged may readily be derived.)

We have stated that (70) has certain advantages from the point of view of numerical integration. However, it should also be stated that the form (77) will probably be more advantageous for ordinary variational calculations. This is because if one adopts a specific

analytic form of F_ℓ^{χ} , one need only interchange r_1 and r_2 in

the expression to obtain $\tilde{F}_\ell^{\chi}$.

The differences in the $f_\ell^{\prime\pm}$ description from that of F_{ℓ}^{χ}

gives rise to characteristic differences in the formulation of

boundary conditions for scattering problems (cf. the next section).

The restriction of these equations to the atomic case (two

identical particles in a fixed central field) has implicitly been made

by assuming that the potential is a function of the residual coordinates,

$$V = V(r_1, r_2, r_{12}), \tag{78}$$

so that V commutes with the angular momentum and therefore appears

as an additional diagonal term in the radial equations.

The inter-particle distance r_{12} is related to the independent

radial coordinates that we have thus far considered, r_1, r_2, θ_{12} via

the law of cosines:

$$r_{12}{}^2 = r_1{}^2 + r_2{}^2 - 2r_1r_2 \cos \theta_{12}.$$

Alternatively, however, one can consider r_1, r_2, and r_{12} as the

independent coordinates and derive radial equations involving them.

Those coordinates, in fact, have certain advantages since the three

singularities in the potential occur at their null point. As

such they can describe the wave function in the region of close

interaction very well. These variables, therefore, are particularly

suited to calculation of low-lying bound states of two-electron

atoms (where on the whole the electrons are quite close to each other

and to the nucleus) and such successful calculations have been done

ever since the early work of Hylleraas.[1]

When one considers the equation in the form we have previously

given them, involving Θ_{12}, one is naturally led to expand the "radial"

wave function in terms of Legendre polynomials of cos Θ_{12}[11,]. The

expansion is then truncated after some $P_n(\cos \Theta_{12})$ and convergence is

sought as a function of n. In these classes of two electron problems,

this constitutes the idea of configuration interaction in its most

general form. Recently this idea has come under some criticism[13,14,15]

principally because such a relative partial wave expansion necessarily

converges slowly where the electron-electron interaction is large

(r_{12} small). The argument is doubtless justified for the above-

mentioned low-lying bound states. However the argument can easily

get distorted and exaggerated, for instance when applied to the

low-energy scattering of electrons from hydrogen.[14] The point there

is that the long-range correlation coming from the induced potential

in the atom is at least as important as the short range correlations[16]

and yet is only poorly approximated by the conventional Hylleraas

type of expansion. This situation has been discussed elsehwere[12].

These reservations notwithstanding, however, it is nevertheless

true that the most accurate three body calculations have been made

using the r_1, r_2, r_{12} coordinates, or linear combinations of them[17],

on·the low-lying states of helium[18] and its isoelectronic ions[17].
We therefore give below the radial equations in terms of r_1, r_2, r_{12}.
The equations are in their asymmetric form corresponding to Eq. (77),
since it is assumed that they will be utilized in connection with
variational calculations with analytic expansions of the radial wave
functions.

$$
\left[L_{r_{12}} + \frac{2m}{\hbar^2}(E-V) \right] F_\ell^{\varkappa} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left[\left\{ \left(\frac{\ell(\ell+1) - \varkappa^2}{\rho^2} \right) 2 r_1^2 r_2^2 + \frac{\varkappa^2}{4} \right\} F_\ell^{\varkappa} \right.
$$

$$
- \delta_{1,\varkappa} (1 - 2 A_\varkappa^\ell)(r_1^2 + r_2^2 - r_{12}^2) \frac{r_1 r_2}{\rho^2} \widetilde{F}_\ell^{\varkappa}
$$

$$
+ (\varkappa+1)(\varkappa+2) \, \beta_{\ell,\varkappa+2} (r_1^2 + r_2^2 - r_{12}^2) \frac{2 r_1 r_2}{\rho^2} \left\{ F_\ell^{\varkappa+2} - \delta_{2,\varkappa+2} \frac{(F_\ell^{\varkappa+2} - \widetilde{F}_\ell^{\varkappa+2})}{2} \right\}
$$

$$
+ \frac{A_{\varkappa-2}^\ell \, A_{\varkappa-1}^\ell (r_1^2 + r_2^2 - r_{12}^2) \, r_1 r_2}{2 \beta_{\ell\varkappa} [1 + \delta_{9,\varkappa-2}(\sqrt{2}-1)] \cdot \rho^2} \left\{ F_\ell^{\varkappa-2} + \delta_{0,\varkappa-2} (2 \widetilde{F}_\varkappa^{\varkappa-2} + F_\ell^{\varkappa-2}) \right\} \right]
$$

$$
+ \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \left[\varkappa \cdot \frac{\rho}{2 r_{12}} \frac{\partial \widetilde{F}^{\varkappa}}{\partial r_{12}} - \varkappa \left\{ \frac{1}{2} \cdot \frac{r_1^2 + r_2^2 - r_{12}^2}{\sqrt{r_1 r_2 [r_{12}^2 - (r_1 - r_2)^2]}} - \frac{r_1^2 + r_2^2 - r_{12}^2 + r_1 r_2}{\rho} \right\} \widetilde{F}_\ell^{\varkappa} \right.
$$

$$
+ (\varkappa+1)(\varkappa+2) \, \beta_{\ell,\varkappa+2} \frac{2 r_1 r_2}{\rho} \left\{ - \widetilde{F}_\ell^{\varkappa+2} + \delta_{2,\varkappa+2} \frac{1}{2} (F_\ell^{\varkappa+2} + \widetilde{F}_\ell^{\varkappa+2}) \right\}
$$

$$
+ \frac{A_{\varkappa-2}^\ell \, A_{\varkappa-1}^\ell \quad r_1 r_2}{2 \beta_{\ell\varkappa} [1 + \delta_{9,\varkappa-2}(\sqrt{2}-1)]} \cdot \frac{1}{\rho} \left\{ \widetilde{F}_\ell^{\varkappa-2} + \delta_{0,\varkappa-2}(2 F_\ell^{\varkappa+2} + \widetilde{F}^{\varkappa-2}) \right\} \quad ;
$$

$$
- \delta_{1,\varkappa}(1 - 2 A_\varkappa^\ell) \frac{r_1 r_2}{\rho} F^{\varkappa} \right] = 0
$$

$$
\tag{79}
$$

Here

$$\rho = + \left[r_{12}^4 - (r_1^2 - r_2^2)^2 + 2 r_{12}^2 (r_1^2 + r_2^2) \right]^{\frac{1}{2}} \tag{80}$$

The quantity whose square root ρ is can easily be shown to be positive definite. In the equation (68) the F_ℓ^χ is understood to be a function of r_1, r_2, r_{12}:

$$F_\ell^\chi = F_\ell^\chi (r_1, r_2, r_{12})$$

In addition $L_{r_{12}}$ is the kinetic energy counterpart of the S-wave $L_{\theta_{12}}$ in terms of r_1, r_2, r_{12}:

$$L_{r_{12}} = \frac{1}{r_1} \frac{\partial^2 r_1}{\partial r_1^2} + \frac{1}{r_2} \frac{\partial^2 r_2}{\partial r_2^2} + \frac{2}{r_{12}} \frac{\partial^2 r_{12}}{\partial r_{12}^2}$$
$$+ \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_2} \cdot \frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_1 r_2} \cdot \frac{\partial^2}{\partial r_2 \partial r_{12}} \tag{81}$$

The equations (79) can readily be put in the form of coupled equations for a given χ . In that form they would be closest to the form originally given by Holmberg[6], (although as we have stated his equations apply to three equal mass particles). One salient difference between the two sets of equations, however, is that the present ones are manifestly real, whereas one term in Holmberg's equations is imaginary[6]. It is clear that the equations as well as the solutions must be reducible to completely real form for any given angular momentum state. The accomplishment of this in the

present case comes from the explicit construction of real vector spherical harmonics, Eq. (49).

VIII BOUNDARY CONDITIONS FOR SCATTERING

In this section we derive the asymptotic forms of the radial functions corresponding to the scattering of an electron from a one electron atom in its ground state. The Coulomb modifications when the target system is an ion instead of an atom can readily be made and will have no effect on the angular integrations with which we are here concerned.

As we have seen in the foregoing sections culminating in the last section, the selection of a symmetric choice of Euler angles (Holmberg's angles) has allowed for a completely general derivation of the radial equations. From the point of view of a scattering problem, however, a symmetric choice of angles is not the most advantageous since here we are concerned with an intrinsically asymmetric situation. Thus if we consider that region of configuration space where r_1 is large and r_2 small, corresponding to electron 1 being scattered from the atom to which electron 2 is bound, the wave function _in this region alone_ will not be symmetric. However in terms of the Hylleraas-Breit angles, the spherical angles of one of the particles being defined as two of the Euler angles, the wave function in this asymmetric region is easier to describe. Nevertheless this is a complication of detail only, since all the angular integrations may readily be performed as we shall now show.

We start with the statement that the complete wave function must have the asymptotic form:

$$\lim_{r_1 \to \infty} \Psi_{\ell 0}(\vec{r}_1, \vec{r}_2) = \frac{\sin(\kappa r_1 + \delta_\ell - \ell\frac{\pi}{2})}{r_1} Y_{\ell 0}(\Omega_1) \frac{R_{1s}(r_2)}{r_2} Y_{00}(\Omega_2) \tag{82}$$

where $(R_{1s}(r_2)/r_2)\, Y_{oo}(\Omega_2)$ is the ground state of the one-electron atom (hydrogen). On the other hand, from Eq. (51),

$$\lim_{r_1 \to \infty} \Psi_{\ell 0}(\vec{r}_1, \vec{r}_2) = \frac{\sin(\kappa r_1 + \delta_\ell - \ell\frac{\pi}{2})}{r_1} \frac{R_{1s}(r_2)}{r_2} \sum_\chi {}''\left[\alpha_\ell^{\chi+}(\theta_{12}) \mathcal{Y}_\ell^{\chi+}(\theta,\Phi,\psi) \right.$$
$$\left. + \alpha_\ell^{\chi-}(\theta_{12}) \mathcal{Y}_\ell^{\chi-}(\theta,\Phi,\psi) \right] \tag{83}$$

where

$$\alpha_\ell^{\chi\pm}(\theta_{12}) = Y_{oo}\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \mathcal{Y}_\ell^{\chi\pm}(\theta,\Phi,\psi) Y_{\ell 0}(\vartheta_1) \sin\theta\, d\theta\, d\Phi\, d\psi \tag{84}$$

It should be noted that (82) refers to the state of parity $(-1)^\ell$ as long as we are considering elastic scattering from the ground (1s) state. This then defines the evenness or oddness of the values over which χ goes in the summation in Eq. (83).

The quadrature in (84) can readily be performed by recalling from Section II that ϑ_1 is the angle between $\hat{z}$ and $\hat{r}_1$ whose spherical angles in the primed coordinate systems are given in Eq. (20). One can then use these spherical angles to expand $P_\ell(\cos \vartheta_1)$ via the addition theorems for spherical harmonics.

In its real form[9] this gives in the present case

$$P_\ell(\nu_1) = P_\ell(\pi/2) P_\ell(\theta) + 2\sum_{m=1}^{\ell}(-1)^m \frac{(\ell-m)!}{(\ell+m)!} P_\ell^m(\pi/2) P_\ell^m(\theta) \cos\left(m(\psi - \tfrac{1}{2}\theta_{12})\right) \tag{85}$$

In (85) we have written both the Legendre and associated Legendre polynomials as functions of the angle but what we mean in all cases is that the angle is to be substituted into the transcendental form of the function. For example $P_1(\beta) = \cos\beta$ and not $P_1(\beta) = \beta$. The sign of the P_ℓ^m is that of Magnus and Oberhettinger[9] (which differs by $(-1)^m$ from that of Morse and Feshbach[3]). To complete the quadrature in (84) we note that

$$d_\ell^{o,\varkappa}(\theta) = (-1)^\varkappa \left[\frac{(\ell-\varkappa)!}{(\ell+\varkappa)!}\right]^{\frac{1}{2}} P_\ell^\varkappa(\theta) \tag{86}$$

Substitution into (84) now yields the desired result:

$$\alpha_\ell^{\varkappa+}(\theta_{12}) = P_\ell^\varkappa(\tfrac{\pi}{2}) \left[\frac{(\ell-\varkappa)!}{(\ell+\varkappa)!}\right]^{\frac{1}{2}} \left\{\delta_{0,\varkappa} + (1-\delta_{0,\varkappa}) \cos\tfrac{1}{2}\theta_{12}\right\} \tag{87a}$$

$$\alpha_\ell^{\varkappa-}(\theta_{12}) = P_\ell^\varkappa(\tfrac{\pi}{2}) \left[\frac{(\ell-\varkappa)!}{(\ell+\varkappa)!}\right]^{\frac{1}{2}} \left\{(1-\delta_{0,\varkappa}) \sin\tfrac{1}{2}\theta_{12}\right\} \tag{87b}$$

$$\vdots$$

The radial function themselves thus approach

$$\lim_{\gamma_1 \to \infty} f_\ell^{\varkappa\pm}(r_1, r_2, \theta_{12}) = \frac{\sin(kr_1 + \delta_\ell - \ell\pi/2)}{r_1} R_{1s}(r_2) \alpha_\ell^{\varkappa\pm}(\theta_{12}) \tag{88}$$

in which form we see that r_1, r_2 dependence of all the $f_\ell^{\chi\pm}$

functions is independent of χ , so that none of them vanishes in

the asymptotic region. Since in all cases the θ_{12} dependence is

trivial, it may be worthwhile to define new functions whose asymptotic

behaviour is strictly the r_1, r_2 dependence in (88).

For bound state problems, it is clear that all the radial func-

tions must vanish in all asymptotic regions.

IX OTHER APPLICATIONS

In addition to two electron atomic or ionic systems the present

equations apply to double mu or pi mesic atoms, although as the mass

of the identical particles gets heavier, the correction for the center

of mass becomes more important. Also for the spinless bosons (pi

mesons) only the space symmetric solutions will presumably be relevant.

The equations can also be applied to two different particles

of the same mass (positron-hydrogen scattering, for example). In

this case, the potential, V, will no longer be symmetric hence the

solutions will not be symmetric which implies that boundary condi-

tions like (72) must be changed to matching conditions of the asym-

metric solutions along the line $r_1 = r_2$[19]. This has the effect of

giving one solution where formerly there were two, in accord with the

distinguishability of the particles.

The major extension of this approach is to two-electron diatomic

molecules. In this case, the extension from one[20] to two elec-

trons is non-trivial.   However, the analysis has been completed

and will be published elsewhere.[21]

Appendix I

In this appendix, we prove the Eqs. (65) and (66). For m = 0,

$\frac{\partial}{\partial \phi}$ terms give zero. Therefore, we can write

$$\Lambda_1 \rightarrow \frac{\partial^2}{\partial \theta^2} - \cot \theta \frac{\partial}{\partial \theta} - \cot^2 \frac{\partial^2}{\partial \psi^2} \tag{I1}$$

$$\Lambda_2 \rightarrow 2 \cot \theta \frac{\partial^2}{\partial \psi \partial \theta} - \frac{\partial}{\partial \psi} - 2 \cot^2 \cdot \frac{\partial}{\partial \psi} \tag{I2}$$

and

$$\partial_\ell^{x+} = N_{\ell x} \cos x \psi \sin^x \theta F_x \tag{I3}$$

$$\partial_\ell^{x-} = N_{\ell x} \sin x \psi \sin^x \theta F_x \tag{I4}$$

where

$$N_{\ell x} = \sqrt{\frac{2\ell+1}{8\pi^2} \cdot \frac{(\ell+x)!}{(\ell-x)!}} \cdot \frac{1}{2^x} \frac{1}{x!} \tag{I5}$$

and

$$F_x = F\left(x-\ell, x+\ell+1, 1+x, \sin^2 \frac{\theta}{2}\right) \tag{I6}$$

Now

$$\Lambda_1 \vartheta_\ell^{\chi+} = N_{\ell\chi} \cos\chi\psi \left[2\chi(\chi-1) \sin^{\chi-2}\theta \cos^2\theta \, F_\chi - \chi \sin\theta \, F_\chi \right.$$

$$\left. + 2\chi \sin^\chi\theta \cos\theta \, A_\chi^\ell \, F_{\chi+1} + \sin^2\theta \, A_\chi^\ell \, A_{\chi+1}^\ell \, F_{\chi+2} \right] \tag{I7}$$

where we have used the well known relations for the derivatives of

hypergeometric functions:

$$\frac{d}{d\theta} F_\chi = A_\chi^\ell \sin\theta \, F_{\chi+1} \tag{I8}$$

$$\frac{d^2}{d\theta^2} F_\chi = A_\chi^\ell \cos\theta \, F_{\chi+1} + A_\chi^\ell \, A_{\chi+1}^\ell \sin^2\theta \, F_{\chi+2} \tag{I9}$$

A relation between F_χ, $F_{\chi+1}$ and $F_{\chi+2}$ can be obtained from

the differential equation satisfied by the hypergeometric function

$$\cos\theta \, F_{\chi+1} = F_\chi - \frac{A_{\chi+1}^\ell \sin^2\theta}{2(\chi+1)} F_{\chi+2} \tag{I10}$$

Using (I10) in (I7), we find

$$\Lambda_1 \vartheta_\ell^{\chi+} = N_{\ell\chi} \cos\chi\psi \left[2\chi(\chi-1) \sin^{\chi-2}\theta \cos^2\theta \, F_\chi \right.$$

$$- \chi \sin^\chi\theta \, F_\chi + 2\chi \sin^\chi\theta \, A_\chi^\ell \, F_\chi \tag{I11}$$

$$\left. + \left(1 - \frac{\chi}{\chi+1}\right) \sin^{\chi+2}\theta \, A_\chi^\ell \, A_{\chi+1}^\ell \, F_{\chi+2} \right]$$

Similarly,

$$\Lambda_2 \partial_\ell^{x+} = -N_{\ell x} \sin x\psi \left[2x(x-1) \sin^{x-2}\theta \cos^2\theta \, F_x - x \sin^x\theta \, F_x \right.$$

$$\left. + 2x A_x^\ell \sin^x\theta \, F_x - \frac{x}{x+1} \sin^{x+2}\theta A_x^\ell A_{x+1}^\ell F_{x+2} \right] \quad (I12)$$

Multiply (I12) by $\sin 2\psi$ and (I11) by $\cos 2\psi$ and subtract to get

$$\left(\sin 2\psi \, \Lambda_2 - \cos 2\psi \, \Lambda_1 \right) \partial_\ell^{x+} = -N_{\ell x} \cos(x-2)\psi \, G - \frac{N_{\ell x}}{2 N_{\ell x+2}} A_x^\ell A_{x+1}^\ell \partial_\ell^{(x+2)+} \quad (I13)$$

where

$$G = \left(2x(x-1) \sin^{x-2}\theta \cos^2\theta - x \sin^x\theta + 2x \sin^x\theta A_x^\ell \right) F_x \quad (I14)$$

$$+ \frac{1-x}{1+x} \sin^{x+2}\theta A_x^\ell A_{x+1}^\ell F_{x+2}$$

Let $x \to x+1$ in (I10), then

$$\cos\theta \, F_{x+2} = F_{x+1} - \sin^2\frac{\theta}{2} \, A^\ell_{x+2} \, F_{x+3}$$

Substituting in the above for F_{x+1} and F_{x+3} by using (I10) we get after some rearrangement

$$\left[\cos^2\theta\left(\frac{x+2}{x+1}\right) + \frac{x+2}{2(x+1)^2}\cdot\sin^2\theta \, A^\ell_{x+1} + \frac{\sin^2\theta \, A^\ell_{x+2}}{2(x+1)}\right] F_{x+2}$$

$$- \frac{\sin^4\theta}{4} \frac{A^\ell_{x+2}\cdot A^\ell_{x+3}}{(x+1)(x+3)} \, F_{x+4} = \frac{x+2}{x+1} F_x$$

Letting $x \to x-2$ multiplying by $2(x-1)^2 \sin^2\theta$ and rearranging we have for $x \geqslant 2$

$$G = 2x(x-1)\sin^{x-2}\theta \, F_{x-2} \qquad\qquad x \neq 0,1 \qquad\qquad \text{(I15)}$$

Also we find directly from (I11) and (I12)

$$G = \frac{1}{2}\sin^2\theta \, A^\ell_0 \, A^\ell_1 \, F_2 \qquad\qquad x = 0 \qquad\qquad \text{(I16)}$$

$$G = -(1-2A^\ell_1)\sin\theta \, F_1 \qquad\qquad x = 1 \qquad\qquad \text{(I17)}$$

Finally then with the substitution of the above in (I13) we obtain for $x \geq 2$

$$(\text{Sin}\, 2\psi\, \Lambda_2 - \text{Cos}\, 2\psi\, \Lambda_1)\, \mathcal{D}_\ell^{\chi +} = -2\chi(\chi-1)\, \beta_{\ell\chi}\, \mathcal{D}_\ell^{(\chi-2)-} - \frac{1}{2}\, \frac{A_\chi^\ell A_{\chi+1}^\ell}{\beta_{\ell\chi+2}}\, \mathcal{D}_\ell^{(\chi+2)+} \tag{I18}$$

where $\beta_{\ell\chi}$ has already been defined in Eq. (68).

The special cases $\chi = 0, 1$ can be determined from (I13), (I16), (I17). With proper normalization

$$(\text{Sin}\, 2\psi\, \Lambda_2 - \text{Cos}\, 2\psi\, \Lambda_1)\, \mathcal{D}_\ell^{0+} = -\sqrt{2}\, \frac{A_0^\ell A_1^\ell}{\beta_{\ell 2}}\, \mathcal{D}_\ell^{2+} \tag{I19}$$

and

$$(\text{Sin}\, 2\psi\, \Lambda_2 - \text{Cos}\, 2\psi\, \Lambda_1)\, \mathcal{D}_\ell^{1+} = (1 - 2A_1^\ell)\, \mathcal{D}_\ell^{1+} - \frac{A_1^\ell A_2^\ell}{2\beta_{\ell 3}}\, \mathcal{D}_\ell^{3+} \tag{I20}$$

We can combine (I18, I19, I20) to get Eq. (65a).

Similarly, we can prove (65a), (66a), (66b).

Appendix II

For $m \neq 0$, we get, using Eqs. (44) and (64)

$$
\Lambda_1 \, \vartheta_\ell^{m,\kappa} = N_{\ell m \kappa} \, e^{i(m\Phi + \kappa\psi)} \, \mathrm{Sin}^{|\kappa-m|}\tfrac{\theta}{2} \, \mathrm{Cos}^{|\kappa+m|}\tfrac{\theta}{2} \left[\left\{ \left(m^2\left(2 - \mathrm{Sin}^2\tfrac{\theta}{2}\right) - 4\,m\,\kappa\,\mathrm{Cos}\,\theta \right. \right. \right.
$$

$$
\left. + \kappa^2\left(1 + \mathrm{Cos}^2\theta - \mathrm{Sin}^2\tfrac{\theta}{2}\right)\right) \frac{1}{\mathrm{Sin}^2\theta} \quad - \frac{|\kappa+m|}{2}\,\mathrm{tan}^2\tfrac{\theta}{2} - \frac{|\kappa-m|}{2}\,\mathrm{Cot}^2\tfrac{\theta}{2}
$$

$$
\left. - \frac{|\kappa-m||\kappa+m|}{2} \right\} F\!\left(-\ell + \tfrac{\beta}{2} - 1,\; \ell + \tfrac{\beta}{2},\; 1 + |\kappa - m|,\; \mathrm{Sin}^2\tfrac{\theta}{2}\right)
$$

$$
+ 2\left(|\kappa-m|\,\mathrm{Cos}^2\tfrac{\theta}{2} - |\kappa+m|\,\mathrm{Sin}^2\tfrac{\theta}{2} \right) A_{m,\kappa}^\ell \, F\!\left(-\ell + \tfrac{\beta}{2},\; \ell + \tfrac{\beta}{2} + 1,\; 2 + |\kappa-m|,\; \mathrm{Sin}^2\tfrac{\theta}{2}\right)
$$

$$
\left. + \mathrm{Sin}^2\theta \, A_{m,\kappa}^\ell \cdot C_{m,\kappa}^\ell \; F\!\left(-\ell + \tfrac{\beta}{2} + 1,\; \ell + \tfrac{\beta}{2} + 2,\; 3 + |\kappa-m|,\; \mathrm{Sin}^2\tfrac{\theta}{2}\right) \right]
$$

$$
\tag{II1}
$$

and

$$
\Lambda_2 \, \vartheta_\ell^{m,\kappa} = i\,N_{\ell m \kappa} \, e^{i(m\Phi + \kappa\psi)} \, \mathrm{Sin}^{|\kappa-m|}\tfrac{\theta}{2} \cdot \mathrm{Cos}^{|\kappa+m|}\tfrac{\theta}{2} \left[\left\{ \frac{2\,m\,\mathrm{Cos}\,\theta - \kappa(1 + \mathrm{Cos}^2\theta)}{\mathrm{Sin}^2\theta} \right. \right.
$$

$$
\left. + \frac{\kappa\,\mathrm{Cos}\,\theta - m}{\mathrm{Sin}\,\theta}\left(|\kappa-m|\,\mathrm{Cot}\tfrac{\theta}{2} - |\kappa+m|\,\mathrm{tan}\tfrac{\theta}{2}\right) \right\} \times
$$

$$
\tag{II2}
$$

$$
F\!\left(-\ell + \tfrac{\beta}{2} - 1,\; \ell + \tfrac{\beta}{2},\; 1 + |\kappa-m|,\; \mathrm{Sin}^2\tfrac{\theta}{2}\right)
$$

$$
\left. + 2(\kappa\,\mathrm{Cos}\,\theta - m)\, A_{m,\kappa}^\ell \, F\!\left(-\ell + \tfrac{\beta}{2},\; \ell + \tfrac{\beta}{2} + 1,\; 2 + |\kappa-m|,\; \mathrm{Sin}^2\tfrac{\theta}{2}\right) \right]
$$

where

$$A^{\ell}_{m,k} = \frac{(-\ell + \frac{\beta}{2} - 1)(\ell + \beta/2)}{2(1 + |k - m|)} \qquad (II3)$$

$$C^{\ell}_{m,k} = \frac{(-\ell + \beta/2)(\ell + \beta/2 + 1)}{2(2 + |k - m|)} \qquad (II4)$$

For illustration purposes, let $k - 2 > m$. Multiply (II2) by $\sin 2\psi$ and (II1) by $\cos 2\psi$ and subtract to get

$$(\sin 2\psi \, \Lambda_2 - \cos 2\psi \, \Lambda_1) \, \partial^{m,k}_{\ell} = -N_{\ell m k} \, e^{im\phi} \cdot \frac{\sin^k \theta}{2^k} \, \cot \frac{\theta}{2} \left[e^{i(k+2)\psi} \cdot \frac{\sin^2 \theta}{2} \right.$$

$$A^{\ell}_{m,k} \, C^{\ell}_{m,k} \, F(-\ell + k + 2, \ \ell + k + 3, \ 3 + k - m, \ \sin^2 \tfrac{\theta}{2}) \ +$$

$$e^{i(k-2)\psi}\left\{ \left(\frac{2(k\cos\theta - m)(\cos\theta(k-1) - m) - k^2 \sin^2\theta}{\sin^2\theta} \ + \right. \right.$$

$$\left. \frac{2(k\cos\theta - m)(1 + k - m) \, A^{\ell}_{m,k}}{\cos\theta(1+k) - m} \right) F(-\ell + k, \ \ell + k + 1, \ 1 + k - m, \ \sin^2 \tfrac{\theta}{2}) \qquad (II5)$$

$$+ \ \frac{(1-k)\cos\theta + m}{2[(k+1)\cos\theta - m]} \cdot \sin^2\theta \, A^{\ell}_{m,k} \, C^{\ell}_{m,k} \, F(-\ell + k + 2, \ell + k + 3, 3 + k - m, \sin^2 \tfrac{\theta}{2}) \left.\left.\right\} \right]$$

where we have used the relation

$$F(-\ell + k + 1, \ell + k + 2, 2 + k - m, \sin^2 \tfrac{\theta}{2}) = \frac{1 + k - m}{\cos\theta(1+k) - m} F(-\ell + k, \ell + k + 1, 1 + k - m, \sin^2 \tfrac{\theta}{2})$$

$$- \operatorname{Sin}^2\tfrac{\theta}{2} \ C^\ell_{m,k} \ F(-\ell+k+2, \ \ell+k+3, \ 3+k-m, \ \operatorname{Sin}^2\tfrac{\theta}{2}) \qquad (II6)$$

Using this result, (which reduces to (I15) for m = 0) in (II5), we obtain for $k \neq 0,1$

$$\left[2(k\cos\theta - m)(\cos\theta(k-1) - m) \ + \ \frac{\operatorname{Sin}^2\theta \ (k+1-m)(2k\cos\theta - 2m)}{\cos\theta(1+k) - m} A^\ell_{m,k} \right.$$

$$\left. - k\operatorname{Sin}^2\theta \right] F(-\ell+k, \ \ell+k+1, \ 1+k-m, \ \operatorname{Sin}^2\tfrac{\theta}{2})$$

$$\qquad (II7)$$

$$- \ \frac{\cos\theta(k-1) - m}{\cos\theta(k+1) - m} \cdot \operatorname{Sin}^4\tfrac{\theta}{2} \ A^\ell_{m,k} \ C^\ell_{m,k} \ F(-\ell+k+2, \ell+k+3, 3+k-m, \operatorname{Sin}^2\tfrac{\theta}{2})$$

$$= \ 2(k-m)(k-1-m) F(-\ell+k-2, \ \ell+k-1, \ k-m-1, \ \operatorname{Sin}^2\tfrac{\theta}{2}),$$

so that

$$\left(\operatorname{Sin}2\psi \, \Lambda_2 - \cos 2\psi \, \Lambda_1 \right) \mathcal{D}^{m,k}_\ell = -2(k-m)(k-m-1) B^m_{\ell k} \mathcal{D}^{m,k-2}_\ell - \frac{A^\ell_{m,k} C^\ell_{m,k}}{2 B^m_{\ell k+2}} \mathcal{D}^{m,k+2}_\ell \qquad (II8)$$

where

$$B^m_{\ell k} \ = \ \frac{N_{\ell m k}}{4 N_{\ell m k-2}} \ = \ \frac{\left[(\ell+k)(\ell+k-1)(\ell+k+2)(\ell-k+1) \right]^{\frac{1}{2}}}{4 \ (k-m)(k-m-1)} \qquad (II9)$$

It is easily verified that

$$(k-m)(k-m-1) B_{\ell k}^{m} = k(k-1) B_{\ell k} \tag{II10}$$

$$\frac{A_{m,k}^{\ell} \cdot C_{m,k}^{\ell}}{B_{\ell k+2}^{m}} = \frac{A_{,k}^{\ell} A_{k+1}^{\ell}}{B_{\ell k}} \tag{II11}$$

Using (II10) and (II11) in (II8), we find

$$\left(\sin 2\psi \, \Lambda_2 - \cos 2\psi A_1\right) \mathcal{D}_{\ell}^{m,k} = -2 k(k-1) B_{\ell k} \mathcal{D}_{\ell}^{m,k-2} - \frac{A_{k}^{\ell} A_{k+1}^{\ell}}{2 B_{\ell k+2}} \mathcal{D}_{\ell}^{m,k+2} \tag{II12}$$

Similarly, we find

$$\left(\sin 2\psi \, \Lambda_2 - \cos 2\psi \, \Lambda_1\right) \mathcal{D}_{\ell}^{m,-k} = -2 k(k-1) B_{\ell k} \mathcal{D}_{\ell}^{m,-(k-2)} - \frac{A_{k}^{\ell} A_{k+1}^{\ell}}{2 B_{\ell k+2}} \mathcal{D}_{\ell}^{m,-(k+2)} \tag{II13}$$

Adding (II12) and (II13) and using the definition (54a) we derive

finally for $\quad \chi \neq 0, 1$

$$\left(\sin 2\psi \; \Lambda_2 - \cos 2\psi \; \Lambda_1\right) \mathcal{D}_\ell^{m, \chi +} = -2\chi(\chi-1)\beta_{\ell\chi} \mathcal{D}_\ell^{m, (\chi-2)+} - \frac{A_\chi^\ell A_{\chi+1}^\ell}{2\beta_{\ell\chi+2}} \mathcal{D}_\ell^{m, (\chi+2)+} \qquad (II14)$$

which is identical in form to (I18) for m = 0.   Other relations can be proved in the same way, thus the radial equations are in fact independent of m.

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Table 1 : Coefficients of the Angular Derivatives in the Kinetic

Energy[a] Cf. Eq. (49)

Coefficient	Derivative	Coefficient	Derivative
$\dfrac{\sin^2(\psi + \frac{\theta_{12}}{2})}{\sin^2\theta_{12}}$	$\dfrac{\partial^2}{\partial\theta^2}$	$\cot\theta_{12}$	$\dfrac{\partial}{\partial\theta_{12}}$
$\dfrac{\cos^2(\psi + \frac{\theta_{12}}{2})}{\sin^2\theta_{12}\sin^2\theta}$	$\dfrac{\partial^2}{\partial\phi^2}$	$\dfrac{-\sin(2\psi + \theta_{12})}{\sin^2\theta_{12}\sin\theta}$	$\dfrac{\partial^2}{\partial\theta\partial\psi}$
A_1	$\dfrac{\partial^2}{\partial\psi^2}$	$\dfrac{\cot\theta\sin(2\psi+\theta_{12})}{\sin^2\theta_{12}}$	$\dfrac{\partial^2}{\partial\theta\partial\psi}$
1	$\dfrac{\partial^2}{\partial\theta_{12}^2}$	0	$\dfrac{\partial^2}{\partial\theta\partial\theta_{12}}$
$\dfrac{\cot\theta\cos^2(\psi+\frac{\theta_{12}}{2})}{\sin^2\theta_{12}}$	$\dfrac{\partial}{\partial\theta}$	$\dfrac{-2\cos\theta\cos^2(\psi+\frac{\theta_{12}}{2})}{\sin^2\theta_{12}\sin^2\theta}$	$\dfrac{\partial^2}{\partial\phi\partial\psi}$
$\dfrac{\cos\theta\sin(2\psi+\theta_{12})}{\sin^2\theta\sin^2\theta_{12}}$	$\dfrac{\partial}{\partial\phi}$	0	$\dfrac{\partial^2}{\partial\phi\partial\theta_{12}}$
B_1	$\dfrac{\partial}{\partial\psi}$	-1	$\dfrac{\partial^2}{\partial\psi\partial\theta_{12}}$

a A_1 and B_1 are given in Eqs. (60) and (61).

Figure Caption

Figure 1.   Perspective drawing of (Holmberg's) Euler angles

and the unit vectors of the problem.

$$\frac{\hat{r}_2 - \hat{r}_1}{2 \sin \frac{\theta_{12}}{2}}$$