Symmetric Euler-Angle Decomposition of the Two-Electron Fixed-Nucleus Problem

A. K. BHATIA,* A. TEMKIN

Theoretical Division, Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, Maryland

I. INTRODUCTION

The decomposition of the Laplacian operator,

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

where the coefficient of the second term is proportional to the square of the angular momentum operator, is the basic relation between kinetic 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

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

in which form it is clear that the effect of this decomposition is to reduce the Schrödinger equation with a spherically symmetric potential from a three-dimensional partial differential equation to a one-dimensional (ordinary) differential equation. As such, this relation is of fundamental mathematical importance.

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 eigenfunctions 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 coordinates 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_1–r_2 plane. Breit's remaining coordinates were chosen as r_1, r_2, and θ_{12}, the latter being the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. To describe two-electron atoms or ions in the approximation that the nuclei are fixed, one has an additional requirement of which there is no analog in the one-body problem. That is the Pauli principle: 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 herein after 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 the 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]

Actually a more symmetrical choice of Euler angles has in the interim been carried out by at least three groups independently of each other. The first treatment is due to Holmberg[6] and applies to three particles of the same mass of which two are identical.[7] A later treatment due to Diehl *et al.*[6] is identical as concerns

* National Academy of Sciences—National Research Council Resident Research Associate.

[1] E. A. Hylleraas, Z. Physik **48**, 469 (1928); **54**, 347 (1929).

[2] G. Breit, Phys. Rev. **35**, 569 (1930).

[3] A clear exposition of Breit's work is contained in P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1719 *et seq.*

[4] U. Fano, private communication. One of us (A.T.) acknowledges valuable discussions with Dr. Fano in 1959 at the outset of the formulation of these ideas.

[5] The D-wave equations in H-B angles have been worked out by H. Feshbach, M.I.T. thesis, 1942 (unpublished) and by one of us, A. Temkin, 1959 (unpublished). The wave functions for several states have been derived by C. Schwartz, Phys. Rev. **123**, 1700 (1961).

[6] B. Holmberg, Kgl. Fysiograf. Sällskap. Lund Förh. **26**, 135 (1956). G. H. Derrick and J. M. Blatt, Nucl. Phys. **8**, 310 (1958). G. H. Derrick, *ibid.* **16**, 405 (1960). H. Diehl, S. Flügge, U. Schröder, A. Völkel, and A. Weiguny, Z. Physik **162**, 1 (1961).

[7] The characteristic of the three (or more) body problem of finite masses is that six coordinates can be eliminated, the three additional constants of the motion coming from the center of mass. Two papers dealing with the elimination of the six coordinates of rotation and translation from a system of N particles are: J. O. Hirschfelder and E. Wigner, Proc. Natl. Acad. Sci. U.S. **21**, 113 (1935); C. F. Curtiss, J. O. Hirschfelder, and F. T. Adler, J. Chem. Phys. **18**, 1638 (1950).

the choice of Euler angles but applies to the three-body problem in general. The case when two of the particles are identical is thus a special case of their results, and they are more detailed concerning the transformation properties of the Euler angles under exchange. To the extent that all these results were meant to apply to the three-nucleon problem, Derrick and Blatt[6] have carried out the most realistic analysis in that account is taken of a force which is considerably more complicated than a simple central force between pairs of particles. Thus in their treatment the orbital angular momentum is not conserved, and the only constants of the motion are parity, the total angular momentum, and the isotopic spin.[6]

Two of the Euler angles that all these groups used are essentially Θ and Φ (Sec. II). Their third angle Ψ, however, is related to moments of inertia of the two identical particles relative to the third. As such it depends on the lengths of the vectors of the problem. As opposed to this our own choice of Ψ depends only on the unit vectors of the problem, nevertheless both sets of Euler angles have virtually the same transformation properties under exchange. Since the basic decomposition is in terms of separable products of radial (length-dependent) and angular variables, it is our opinion that the previously defined Ψ, which appears to contain a subtle connection between the angular and radial parts, is less advantageous than our own, in which the separability is maintained on all levels.

The present paper also treats the case of two identical particles in the field of an infinitely heavy nucleus. In a certain sense this problem stands in the same relation to the general three-body problem as the one-body problem is related to the relative motion of the two-body problem. With the addition of exchange, which we have stated is a nontrivial problem, we attempt here to make the theoretical framework of the reduction to radial equations as accessible as the corresponding reduction in the one-body problem is, even to the nonspecialist. On a practical level the results of this investigation apply most directly to two-electron atoms and ions and the associated scattering problems (Sec. IX).

In Sec. III we explain as lucidly as we can the transformation properties of our Euler angles and the consequent transformation properties of the vector spherical harmonics. The latter in our terminology are the eigenfunctions of the total angular momentum, and in Sec. IV we derive the angular momentum operators in a straightforward way. These eigenfunctions even with their concomitant transformation properties are still not eigenfunctions of exchange. Since exchange commutes with all the other constants of the motion, it is possible to construct simultaneous eigenfunctions of exchange. Complete exchange, however, acts on the radial coordinates as well as the Euler angles. In Sec. V, therefore, we show how the exchange vector spherical harmonics are combined with the functions of the

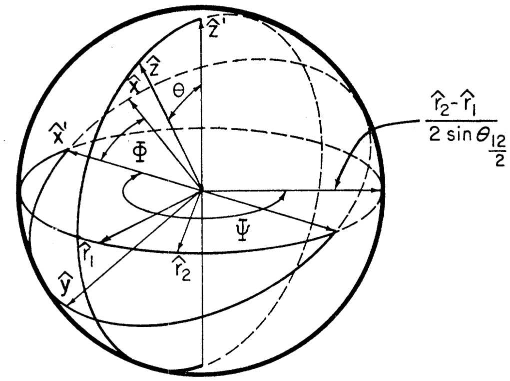

FIG. 1. Perspective drawing of the Euler angles and the unit vectors of the problem.

residual coordinates to give a total spatial wave function which is either symmetric (singlet) or antisymmetric (triplet) under exchange. The derivation of the kinetic energy in terms of the radial and (Eulerian) angle coordinates is the last remaining step (Sec. VI) before the derivation of the radial equations themselves. The results of Sec. VI are necessarily quite tediously derived. Our aim has been to give enough of the derivation and results (parts of which are included in the appendices) to allow our formulas to be checked as mechanically as possible.

When the kinetic energy has been put in suitable form, the derivation of the radial equations for arbitrary angular momentum (Section VII) is a comparatively simple matter. One salient improvement of the present radial equations over those of Holmberg[6] and Diehl *et al.*[6] is that ours are completely real. The radial equations are a finite set of coupled three-dimensional partial differential equations which can be written in various forms and in two major sets of radial coordinates. Most of the various possibilities are in fact given in Sec. VII. Any of the various possibilities constitute a rigorous decomposition of the Schrödinger equation. In addition to the usual bound-state problems, the partial waves for the scattering of electrons from one-electron atoms or ions are also governed by these equations. We have therefore worked out the boundary conditions for the relevant electron–atom (ion) scattering in these coordinates (Sec. VIII).

II. THE EULER ANGLES

Figure 1 contains a perspective drawing of the Euler 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

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

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

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

As is usual, a caret on a symbol is used to represent a unit *vector* in the given direction. In particular $\hat{\imath}$, $\hat{\jmath}$, $\hat{k}$ 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 $\hat{\imath}'$, $\hat{\jmath}'$, $\hat{k}'$ and $\hat{x}'$, $\hat{y}'$, $\hat{z}'$ are identical.

The 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:

$$0 \le \Theta \le \pi, \quad \text{in } z\text{–}z' \text{ plane};$$

$$0 \le \Phi \le 2\pi, \quad \text{in } x\text{–}y \text{ plane};$$

$$0 \le \Psi \le 2\pi, \quad \text{in } x'\text{–}y' \text{ plane}.$$

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

$$\hat{x}' = \hat{\imath}\cos\Phi + \hat{\jmath}\sin\Phi. \tag{7}$$

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 $\frac{3}{2}\pi+\Phi$ (cf. Fig. 1). The polar angle of $\hat{z}'$ is clearly Θ; therefore, we have the important relation:

$$\hat{z}' = \hat{\imath}\sin\Theta\sin\Phi - \hat{\jmath}\sin\Theta\cos\Phi + \hat{k}\cos\Theta. \tag{8}$$

The relations between the Euler angles and the spherical angles of the individual particles are obtained by substituting Eqs. (7) and (8) into the left-hand side of Eqs. (1) and (2) and using the ordinary decomposition of $\hat{r}_1$ and $\hat{r}_2$ in the right-hand side: One obtains

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

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

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

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

$$2\sin(\theta_{12}/2)\sin\Psi = (\cos\vartheta_2 - \cos\vartheta_1)\sin\Theta + [\sin\vartheta_2\sin(\varphi_2-\Phi) - \sin\vartheta_1\sin(\varphi_1-\Phi)]\cos\Theta, \tag{13}$$

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

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 $\hat{r}_1$ and $\hat{r}_2$ in the particle plane (primed coordinate system):

$$\hat{r}_1 = \hat{\imath}'\sin(\Psi - \tfrac{1}{2}\theta_{12}) - \hat{\jmath}'\cos(\Psi - \tfrac{1}{2}\theta_{12}), \tag{15}$$

$$\hat{r}_2 = \hat{\imath}'\sin(\Psi + \tfrac{1}{2}\theta_{12}) - \hat{\jmath}'\cos(\Psi + \tfrac{1}{2}\theta_{12}), \tag{16}$$

$$\hat{z} = \hat{\jmath}'\sin\Theta + \hat{k}'\cos\Theta, \tag{17}$$

$$\hat{y} = \hat{\imath}'\sin\Phi + \hat{\jmath}'\cos\Theta\cos\Phi - \hat{k}'\sin\Theta\cos\Phi, \tag{18}$$

$$\hat{x} = \hat{\imath}'\cos\Phi - \hat{\jmath}'\cos\Theta\sin\Phi + \hat{k}'\sin\Theta\sin\Phi. \tag{19}$$

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

$$\cos\vartheta_1 = -\sin\Theta\cos(\Psi - \tfrac{1}{2}\theta_{12}), \tag{20a}$$

$$\cos\vartheta_2 = -\sin\Theta\cos(\Psi + \tfrac{1}{2}\theta_{12}), \tag{20b}$$

$$\sin\vartheta_1\cos\varphi_1 = \cos\Phi\sin(\Psi - \tfrac{1}{2}\theta_{12}) + \cos\Theta\sin\Phi\cos(\Psi - \tfrac{1}{2}\theta_{12}), \tag{21a}$$

$$\sin\vartheta_2\cos\varphi_2 = \cos\Phi\sin(\Psi + \tfrac{1}{2}\theta_{12}) + \cos\Theta\sin\Phi\cos(\Psi + \tfrac{1}{2}\theta_{12}), \tag{21b}$$

$$\sin\vartheta_1\sin\varphi_1 = \sin\Phi\sin(\Psi - \tfrac{1}{2}\theta_{12}) - \cos\Theta\cos\Phi\cos(\Psi - \tfrac{1}{2}\theta_{12}), \tag{22a}$$

$$\sin\vartheta_2\sin\varphi_2 = \sin\Phi\sin(\Psi + \tfrac{1}{2}\theta_{12}) - \cos\Theta\cos\Phi\cos(\Psi + \tfrac{1}{2}\theta_{12}). \tag{22b}$$

III. PROPERTIES UNDER PARITY AND EXCHANGE

The operation of parity corresponds to the simultaneous inversion of both particles' coordinates: $\mathbf{r}_1 \to -\mathbf{r}_1$, $\mathbf{r}_2 \to -\mathbf{r}_2$. It can be seen from Fig. 1 that this places $\hat{r}_1$ and $\hat{r}_2$ 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 $\hat{x}'$ will not change. On the other hand $(\hat{r}_2 - \hat{r}_1)$

goes into the negative of itself, so that Ψ gets increased by π. In other words under *parity*

$$\Theta\rightarrow\Theta,$$
$$\Phi\rightarrow\Phi,$$
$$\Psi\rightarrow\pi+\Psi. \tag{23}$$

Exchange corresponds to the transformation $\mathbf{r}_1\rightleftarrows\mathbf{r}_2$. From the analytical definitions $\hat{z}'$ and $\hat{x}'$, Eqs. (1) and (2), the new primed axes will go into the negative of themselves. Also $(\hat{r}_2-\hat{r}_1)$ goes into negative of itself. Clearly the inversion of the z' axis corresponds to the transformation $\Theta\rightarrow\pi-\Theta$. 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 $\Phi\rightarrow\pi+\Phi$. The simultaneous inversion of $\hat{x}'$ and $(\hat{r}_2-\hat{r}_1)$ 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 of itself, it becomes clear that $\Psi\rightarrow 2\pi-\Psi$. Thus we have under *exchange*

$$\Theta\rightarrow\pi-\Theta,$$
$$\Phi\rightarrow\pi+\Phi,$$
$$\Psi\rightarrow 2\pi-\Psi. \tag{24}$$

The significance of these transformations relates to the transformation properties of the vector spherical harmonics under the same operations. 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

$$\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi)=\frac{[2(2l+1)]^{\frac{1}{2}}}{4\pi}\times\exp[i(m\Phi+k\Psi)]d_l^{m,k}(\Theta), \tag{25}$$

where the normalization has been so chosen that the function is identical with what is given in Sec. IV and the $d_l^{m,k}(\Theta)$ agree with those given by Wigner.[8] Only the dependence on Θ is nontrivial:

$$d_l^{m,k}(\Theta)=(-1)^{\frac{1}{2}[|k-m|+k-m]}\frac{4\pi}{[2(2l+1)]^{\frac{1}{2}}}N_{lmk}\sin^{|k-m|}(\Theta/2)\times\cos^{|k+m|}(\Theta/2)F(-l+\beta/2-1,\; l+\beta/2;1+|k-m|;\sin^2(\Theta/2)), \tag{26}$$

where β and N_{lmk} are defined in Eqs. (45) and (46). $F(a,b;c;z)$ is the hypergeometric function in the notation of Magnus and Oberhettinger.[9] The important property of $d_l^{m,k}(\Theta)$, proved in Wigner's book,[8] is

$$d_l^{m,k}(\pi-\Theta)=(-1)^{l-m}d_l^{m,-k}(\Theta). \tag{27}$$

The phase in (26) is such that this relation holds for all values of m and k.[9a]

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

$$\mathcal{P}\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi)=\mathfrak{D}_l^{m,k}(\Theta,\Phi,\pi+\Psi),$$
$$\mathcal{E}_{12}\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi)=\mathfrak{D}_l^{m,k}(\pi-\Theta,\pi+\Phi,2\pi-\Psi),$$

which using (27) reduce to

$$\mathcal{P}\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi)=(-1)^k\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi), \tag{28}$$
$$\mathcal{E}_{12}\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi)=(-1)^l\mathfrak{D}_l^{m,-k}(\Theta,\Phi,\Psi). \tag{29}$$

The simplicity of Eq. (29) is the essential feature which recommends these 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

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

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[8] E. Wigner, *Group Theory* (Academic Press Inc., New York and London, 1959), p. 216. Cf. also, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1957), Chap. 4.

[9] W. Magnus and I. Oberhettinger, *Formulas and Theorems for the Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949).

[9a] This point is extremely subtle. Usually, the phase factor is given for $m\geq k\geq 0$ for which it is $+1$. For other ranges of m and k the phase is given implicitly by the requirement that $d_l^{m,k}$ obey certain symmetry properties (cf. in particular Edmonds' book, Ref. 8). As far as we know, the explicit form of this phase factor is given for the first time in Eqs. (26) and (44). If this phase is not included, then Eq. (27) is not generally valid. However, that property is essential in constructing wave functions of the proper exchange character. Such an omission was made in the work of Diehl *et al.* (Ref. 6), so that the inferred exchange properties of their radial functions are not completely consistent. However, they are correct if their $\mathfrak{D}$ functions are given the present phase.

where

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

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:

$$A_{\theta_{12}} = 0, \quad (32)$$

$$A_\Theta = -\cos\Phi, \quad (33)$$

$$A_\Phi = \sin\Phi\cot\Theta, \quad (34)$$

$$A_\Psi = -\sin\Phi/\sin\Theta. \quad (35)$$

Thus,

$$M_x = \frac{\hbar}{i}\left[\cos\Phi\frac{\partial}{\partial\Theta} - \sin\Phi\cot\Theta\frac{\partial}{\partial\Phi} + \frac{\sin\Phi}{\sin\Theta}\frac{\partial}{\partial\Psi}\right]. \quad (36)$$

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

$$\partial\vartheta_1/\partial\Phi = \partial\vartheta_2/\partial\Phi = 0, \quad (37)$$

and from (10) and (11)

$$\partial\varphi_1/\partial\Phi = \partial\varphi_2/\partial\Phi = 1. \quad (38)$$

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

$$\partial/\partial\Phi = \partial/\partial\varphi_1 + \partial/\partial\varphi_2.$$

However, since $M_z = (\hbar/i)(\partial/\partial\varphi_1 + \partial/\partial\varphi_2)$, we therefore have the z component of $\mathbf{M}$:

$$M_z = (\hbar/i)\partial/\partial\Phi. \quad (39)$$

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

$$M_y = \frac{\hbar}{i}\left[\sin\Phi\frac{\partial}{\partial\Theta} + \cos\Phi\cot\Theta\frac{\partial}{\partial\Phi} - \frac{\cos\Phi}{\sin\Theta}\cdot\frac{\partial}{\partial\Psi}\right]. \quad (40)$$

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

$$\mathbf{M}^2 = -\hbar^2\left[\frac{\partial^2}{\partial\Theta^2} + \frac{1}{\sin^2\Theta}\left(\frac{\partial^2}{\partial\Phi^2} + \frac{\partial^2}{\partial\Psi^2}\right) + \cot\Theta\frac{\partial}{\partial\Theta} - 2\frac{\cot\Theta}{\sin\Theta}\frac{\partial^2}{\partial\Phi\partial\Psi}\right]. \quad (41)$$

The vector spherical harmonics, which have been given in Eq. (25), are simultaneous eigenfunctions of $\mathbf{M}^2$ and M_z with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$:

$$\mathbf{M}^2\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi) = \hbar^2 l(l+1)\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi), \quad (42)$$

$$M_z\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi) = \hbar m\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi). \quad (43)$$

They are given in a completely general, normalized form in Pauling and Wilson.[10] With Wigner's phase[8,9a] they are explicitly

$$\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi) = (-1)^{\frac{1}{2}[|k-m|+k-m]}N_{lmk}\sin^{|k-m|}(\Theta/2) \times \cos^{|k+m|}(\Theta/2)\exp[i(m\Phi+k\Psi)]\times F(-l+\tfrac{1}{2}\beta-1, l+(\beta/2); 1+|k-m|; \sin^2(\Theta/2)), \quad (44)$$

where

$$\beta = |k+m| + |k-m| + 2 \quad (45)$$

and the normalization constant is

$$N_{lmk} = \left[\frac{(2l+1)(l+\frac{1}{2}|k+m|+\frac{1}{2}|k-m|)!(l-\frac{1}{2}|k+m|+\frac{1}{2}|k-m|)!}{8\pi^2(l-\frac{1}{2}|k+m|-\frac{1}{2}|k-m|)!(l+\frac{1}{2}|k+m|-\frac{1}{2}|k-m|)!}\right]^{\frac{1}{2}}\frac{1}{|k-m|!}. \quad (46)$$

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: $-l \le m, k \le l$. The physical significance of k derives from the fact that the $\mathfrak{D}_l^{m,k}$ 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

[10] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York and London, 1935), p. 280.

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 commute with the total angular momentum. In this case the total wave function for a given l must be a linear superposition of the degenerate $\mathfrak{D}_l^{m,k}$. 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:

$$\Psi_{lm}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{k=-l}^{l} g_l^k(r_1,r_2,\theta_{12})\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi). \quad (47)$$

The parity operation, Eq. (23), only affects the Euler angles, and from Eq. (28) it only multiplies the $\mathfrak{D}_l^{m,k}$ 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:

$$\Psi_{lm}^{\text{even}}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{k\text{ even}}'' g_l^k(r_1,r_2,\theta_{12})\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi), \quad (48a)$$

$$\Psi_{lm}^{\text{odd}}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{k\text{ odd}}'' g_l^k(r_1,r_2,\theta_{12})\mathfrak{D}_l^{m,k}(\Theta,\Phi,\Psi), \quad (48b)$$

where the double prime on the summation emphasizes that the sum goes over every second 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 $\partial/\partial\Phi$ and $\partial/\partial\Psi$. 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

$$\mathfrak{D}_l^{\kappa+}\equiv\frac{\mathfrak{D}_l^{0,\kappa}+(-1)^\kappa\mathfrak{D}_l^{0,-\kappa}}{\sqrt{2}[1+\delta_{0\kappa}(\sqrt{2}-1)]}=\frac{(2l+1)^{\frac12}}{2\pi}\frac{\cos\kappa\Psi d_l^{0,\kappa}(\Theta)}{[1+\delta_{0\kappa}(\sqrt{2}-1)]}, \quad (49a)$$

$$\mathfrak{D}_l^{\kappa-}\equiv\frac{\mathfrak{D}_l^{0,\kappa}-(-1)^\kappa\mathfrak{D}_l^{0,-\kappa}}{i\sqrt{2}}=\frac{(2l+1)^{\frac12}}{2\pi}\sin\kappa\Psi d_l^{0,\kappa}(\Theta), \quad (49b)$$

for $\kappa\geq 0$, where

$$\kappa=|k|. \quad (50)$$

The important property of these linear combinations is that they are eigenfunctions of exchange:

$$\mathcal{E}_{12}\mathfrak{D}_l^{\kappa\pm}=\pm(-1)^{l+\kappa}\mathfrak{D}_l^{\kappa\pm}. \quad (49c)$$

This then constitutes a set of real, orthonormal vector spherical harmonics. These real vector spherical harmonics are still eigenfunctions of parity with eigenvalue $(-1)^\kappa$.

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 advantage of a symmetrical choice of Euler 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

$$\Psi_{l0}(\mathbf{r}_1,\mathbf{r}_2)=\sum_\kappa''[f_l^{\kappa+}(r_1,r_2,\theta_{12})\mathfrak{D}_l^{\kappa+}(\Theta,\Phi,\Psi)+f_l^{\kappa-}(r_1,r_2,\theta_{12})\mathfrak{D}_l^{\kappa-}(\Theta,\Phi,\Psi)], \quad (51)$$

the operation of exchange on this sum then gives, with the use of (49c),

$$\begin{aligned}\mathcal{E}_{12}\Psi_{l0}(\mathbf{r}_1,\mathbf{r}_2)&=\Psi_{l0}(\mathbf{r}_2,\mathbf{r}_1)\\&=\sum_\kappa''[f_l^{\kappa+}(r_2,r_1,\theta_{12})(-1)^{l+\kappa}\mathfrak{D}_l^{\kappa+}(\Theta,\Phi,\Psi)\\&\quad+f_l^{\kappa-}(r_2,r_1,\theta_{12})(-1)^{l+\kappa+1}\mathfrak{D}_l^{\kappa-}(\Theta,\Phi,\Psi)].\end{aligned}$$

Thus, if

$$f_l^{\kappa+}(r_2,r_1,\theta_{12})=\pm(-1)^{l+\kappa}f_l^{\kappa+}(r_1,r_2,\theta_{12}), \quad (52a)$$

$$f_l^{\kappa-}(r_2,r_1,\theta_{12})=\pm(-1)^{l+\kappa+1}f_l^{\kappa-}(r_1,r_2,\theta_{12}), \quad (52b)$$

the function Ψ_{l0} of Eq. (51) is a real, space-symmetric (upper sign) or space-antisymmetric (lower sign), eigenfunction of $\mathbf{M}^2$ 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

$$g_l^\kappa=(1/\sqrt{2})(f_l^{\kappa+}-if_l^{\kappa-}),\qquad \kappa>0, \quad (53a)$$

and

$$g_l^{-\kappa}=[(-1)^\kappa/\sqrt{2}](f_l^{\kappa+}+if_l^{\kappa-}),\qquad \kappa>0; \quad (53b)$$

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

Alternatively one can define generalizations of the $\mathfrak{D}_l^{\kappa\pm}$, Eq. (49), for arbitrary m.

$$\mathfrak{D}_l^{(m,\kappa)+}\equiv[\sqrt{2}+\delta_{0\kappa}(2-\sqrt{2})]^{-1}[\mathfrak{D}_l^{m,\kappa}+(-1)^\kappa\mathfrak{D}_l^{m,-\kappa}]$$

$$\mathfrak{D}_l^{(m,\kappa)-}\equiv(\sqrt{2}i)^{-1}[\mathfrak{D}_l^{m,\kappa}-(-1)^\kappa\mathfrak{D}_l^{m,-\kappa}], \tag{54}$$

where $\mathfrak{D}_l^{(0,\kappa)\pm}=\mathfrak{D}_l^{\kappa\pm}$ for $m=0$. Note for $m\neq0$ that the modified spherical harmonics $\mathfrak{D}_l^{(m,\kappa)\pm}$ are no longer real.

The complete function for arbitrary m can then be written

$$\mathbf{F}_{lm}(\mathbf{r}_1,\mathbf{r}_2)=\sum_\kappa{}''[f_l^{\kappa+}\mathfrak{D}_l^{(m,\kappa)+}+f_l^{\kappa-}\mathfrak{D}_l^{(m,\kappa)-}]. \tag{55}$$

Note that by virtue of the action of the raising and lowering operators (Appendix II), the phase of the individual terms except possibly for an over-all minus sign, is correct as it stands.

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.

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

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

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

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

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

where

$$F_1=\frac{1}{\sin^2\theta_{12}}\left[\sin^2(\Psi+\tfrac{1}{2}\theta_{12})\frac{\partial^2}{\partial\Theta^2}+\cos^2(\Psi+\tfrac{1}{2}\theta_{12})\cot\Theta\frac{\partial}{\partial\Theta}+\cos^2(\Psi+\tfrac{1}{2}\theta_{12})\frac{1}{\sin^2\Theta}\frac{\partial^2}{\partial\Phi^2}+\sin(2\Psi+\theta_{12})\frac{\cot\Theta}{\sin\Theta}\frac{\partial}{\partial\Phi}-\sin(2\Psi+\theta_{12})\frac{1}{\sin\Theta}\frac{\partial^2}{\partial\Theta\partial\Phi}+\sin(2\Psi+\theta_{12})\cot\Theta\frac{\partial^2}{\partial\Psi\partial\Theta}-2\cos^2(\Psi+\tfrac{1}{2}\theta_{12})\frac{\cot\Theta}{\sin\Theta}\frac{\partial^2}{\partial\Psi\partial\Phi}\right]-\frac{\partial^2}{\partial\Psi\partial\theta_{12}}+A_1\frac{\partial^2}{\partial\Psi^2}+B_1\frac{\partial}{\partial\Psi} \tag{59}$$

and

$$A_1=\tfrac{1}{4}+(\cot^2\Theta/\sin^2\theta_{12})\cos^2(\Psi+\tfrac{1}{2}\theta_{12}), \tag{60}$$

$$B_1=(\cos\Psi/\sin^2\theta_{12})\sin(\Psi+\theta_{12})-[\sin(2\Psi+\theta_{12})/\sin^2\theta_{12}\sin^2\Theta]-\tfrac{1}{2}\cot(\tfrac{1}{2}\theta_{12}). \tag{61}$$

The expressions for F_2, A_2, and B_2 can be obtained by replacing θ_{12} by $-\theta_{12}$ in the above formulas (including the appropriate partial derivatives). This is equivalent to operating with $\mathcal{E}_{12}$;

$$F_2(\Theta,\Phi,\Psi,\theta_{12})=F_1(\Theta,\Phi,\Psi,-\theta_{12}). \tag{62}$$

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 $[M_x, \nabla_1^2+\nabla_2^2]=0$.

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.[1–3]

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

TABLE I. Coefficients of the angular derivatives in the kinetic energy.[a] Cf. Eq. (49).

Coefficient	Derivative	Coefficient	Derivative
$\frac{\sin^2(\Psi+\frac{1}{2}\theta_{12})}{\sin^2\theta_{12}}$	$\partial^2/\partial\Theta^2$	$\cot\theta_{12}$	$\partial/\partial\theta_{12}$
$\frac{\cos^2(\Psi+\frac{1}{2}\theta_{12})}{\sin^2\theta_{12}\sin^2\Theta}$	$\partial^2/\partial\Phi^2$	$\frac{-\sin(2\Psi+\theta_{12})}{\sin^2\theta_{12}\sin\Theta}$	$\partial^2/\partial\theta\partial\Phi$
A_1	$\partial^2/\partial\Psi^2$	$\frac{\cot\Theta\sin(2\Psi+\theta_{12})}{\sin^2\theta_{12}}$	$\partial^2/\partial\Theta\partial\Psi$
1	$\partial^2/\partial\theta_{12}^2$	0	$\partial^2/\partial\Theta\partial\theta_{12}$
$\frac{\cot\Theta\cos^2(\Psi+\frac{1}{2}\theta_{12})}{\sin^2\theta_{12}}$	$\partial/\partial\Theta$	$\frac{-2\cos\Theta\cos^2(\Psi+\frac{1}{2}\theta_{12})}{\sin^2\theta_{12}\sin^2\Theta}$	$\partial^2/\partial\Phi\partial\Psi$
$\frac{\cos\Theta\sin(2\Psi+\theta_{12})}{\sin^2\Theta\sin^2\theta_{12}}$	$\partial/\partial\Phi$	0	$\partial_2/\partial\Phi\partial\theta_{12}$
B_1	$\partial/\partial\Psi$	-1	$\partial^2/\partial\Psi\partial\theta_{12}$

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

of operators whose effect on the angular momentum eigenfunctions is particularly simple. One can show

$$F_1=\frac{1}{2\sin^2\theta_{12}}\left[-\frac{1}{\hbar^2}\mathbf{M}^2+\cos\theta_{12}(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)+\sin\theta_{12}(\sin 2\Psi\Lambda_1+\cos 2\Psi\Lambda_2)\right]-\frac{\partial^2}{\partial\theta_{12}\partial\Psi}-\tfrac{1}{2}\cot\theta_{12}\frac{\partial}{\partial\Psi}+\left(\frac{1}{4}-\frac{1}{2\sin^2\theta_{12}}\right)\frac{\partial^2}{\partial\Psi^2}, \quad (63)$$

where

$$\Lambda_1=2\frac{\partial^2}{\partial\Theta^2}+\frac{\partial^2}{\partial\Psi^2}+\frac{1}{\hbar^2}\mathbf{M}^2,$$

$$\Lambda_2=2\frac{\cot\Theta}{\sin\Theta}\frac{\partial}{\partial\Phi}-(1+2\cot^2\Theta)\frac{\partial}{\partial\Psi}-\frac{2}{\sin\Theta}\frac{\partial^2}{\partial\Theta\partial\Phi}+2\cot\Theta\frac{\partial^2}{\partial\Theta\partial\Psi}, \quad (64)$$

and $\mathbf{M}^2$ 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

The essential properties of the combinations of the operators appearing in F_1 and F_2, Eq. (63), are the following (cf. Appendix I):

$$2(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)\mathfrak{D}_l^{\kappa+}=-B_l^{\kappa}(1-\delta_{0\kappa}-\delta_{1\kappa})\mathfrak{D}_l^{(\kappa-2)+}+\delta_{1\kappa}l(l+1)\mathfrak{D}_l^{\kappa+}-(1+\delta_{0\kappa})B_{l,\kappa+2}\mathfrak{D}_l^{(\kappa+2)+}, \quad (65a)$$

$$2(\sin 2\Psi\Lambda_1+\cos 2\Psi\Lambda_2)\mathfrak{D}_l^{\kappa+}=-B_l^{\kappa}(1-\delta_{0\kappa}-\delta_{1\kappa}-\delta_{2\kappa})\mathfrak{D}_l^{(\kappa-2)-}-\delta_{1\kappa}l(l+1)\mathfrak{D}_l^{\kappa-}+(1+\delta_{0\kappa})B_{l,\kappa+2}\mathfrak{D}_l^{(\kappa+2)-}, \quad (65b)$$

$$2(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)\mathfrak{D}_l^{\kappa-}=-B_l^{\kappa}(1-\delta_{0\kappa}-\delta_{1\kappa}-\delta_{2\kappa})\mathfrak{D}_l^{(\kappa-2)-}-\delta_{1\kappa}l(l+1)\mathfrak{D}_l^{\kappa-}-(1-\delta_{0\kappa})B_{l,\kappa+2}\mathfrak{D}_l^{(\kappa+2)-}, \quad (66a)$$

$$2(\sin 2\Psi\Lambda_1+\cos 2\Psi\Lambda_2)\mathfrak{D}_l^{\kappa-}=+B_l^{\kappa}(1-\delta_{0\kappa}-\delta_{1\kappa})\mathfrak{D}_l^{(\kappa-2)+}-\delta_{1\kappa}l(l+1)\mathfrak{D}_l^{\kappa+}-(1-\delta_{0\kappa})B_{l,\kappa+2}\mathfrak{D}_l^{(\kappa+2)+}, \quad (66b)$$

where ($A_{l\kappa}$ is needed in Appendix I)

$$A_{l\kappa}=\frac{(\kappa-l)(\kappa+l+1)}{2(\kappa+1)} \quad (67)$$

and

$$B_{l\kappa}=\frac{[(l-\kappa+1)(l-\kappa+2)(l+\kappa)(l+\kappa-1)]^{\frac{1}{2}}}{[1+\delta_{2\kappa}(\sqrt{2}-1)]}, \quad (68a)$$

$$B_l^{\kappa}=B_{l\kappa}[1+\delta_{2\kappa}(\sqrt{2}-1)]^2. \quad (68b)$$

Recall that κ is the absolute value of k, Eq. (50).

We have proved in Appendix II that these relationships are not altered if one replaces the $\mathfrak{D}_l^{\kappa\pm}$ functions by the $\mathfrak{D}_l^{(m,\kappa)\pm}$ functions of Eq. (54). As such it becomes quite simple to derive the reduced equations from the original Schrödinger equation

$$H\Psi_{lm}=E\Psi_{lm} \tag{69}$$

for any m, and to see that the radial equations are independent of m. One obtains

$$\begin{aligned}\Big[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\Big]f_l^{\kappa+}-\Big(\frac{1}{r_1^2}+\frac{1}{r_2^2}\Big)\\ \times\Big[\Big\{\frac{l(l+1)-\kappa^2}{2\sin^2\theta_{12}}+\frac{\kappa^2}{4}-\frac{\cot\theta_{12}}{4\sin\theta_{12}}l(l+1)\,\delta_{1\kappa}\Big\}f_l^{\kappa+}\\ +\frac{\cot\theta_{12}}{4\sin\theta_{12}}B_l^{\kappa+2}f_l^{(\kappa+2)+}\\ +\frac{\cot\theta_{12}}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa}+\delta_{2\kappa})B_{l\kappa}f_l^{(\kappa-2)+}\Big]\\ +\Big(\frac{1}{r_1^2}-\frac{1}{r_2^2}\Big)\Big[-\kappa\Big(\tfrac{1}{2}\cot\theta_{12}+\frac{\partial}{\partial\theta_{12}}\Big)f_l^{\kappa-}-\frac{l(l+1)}{4\sin\theta_{12}}\delta_{1\kappa}f_l^{\kappa-}\\ +\frac{B_l^{\kappa+2}}{4\sin\theta_{12}}f_l^{(\kappa+2)-}-\frac{1}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa}-\delta_{2\kappa})B_{l\kappa}f_l^{(\kappa-2)-}\Big]\\ =0,\end{aligned} \tag{70a}$$

$$\begin{aligned}\Big[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\Big]f_l^{\kappa-}-\Big(\frac{1}{r_1^2}+\frac{1}{r_2^2}\Big)\\ \times\Big[\Big\{\frac{l(l+1)-\kappa^2}{2\sin^2\theta_{12}}+\frac{\kappa^2}{4}+\frac{\cot\theta_{12}}{4\sin\theta_{12}}l(l+1)\,\delta_{1\kappa}\Big\}f_l^{\kappa-}\\ +\frac{\cot\theta_{12}}{4\sin\theta_{12}}(1-\delta_{0\kappa})B_l^{\kappa+2}f_l^{(\kappa+2)-}\\ +\frac{\cot\theta_{12}}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa}-\delta_{2\kappa})B_{l\kappa}f_l^{(\kappa-2)-}\Big]+\Big(\frac{1}{r_1^2}-\frac{1}{r_2^2}\Big)\\ \times\Big[\kappa\Big(\tfrac{1}{2}\cot\theta_{12}+\frac{\partial}{\partial\theta_{12}}\Big)f_l^{\kappa+}-\frac{l(l+1)}{4\sin\theta_{12}}\delta_{1\kappa}f_l^{\kappa+}\\ -\frac{(1-\delta_{0\kappa})}{4\sin\theta_{12}}B_l^{\kappa+2}f_l^{(\kappa+2)+}\\ +\frac{1}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa}+\delta_{2\kappa})B_{l\kappa}f_l^{(\kappa-2)+}\Big]=0.\end{aligned} \tag{70b}$$

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

$$L_{\theta_{12}}=\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2+\Big(\frac{1}{r_1^2}+\frac{1}{r_2^2}\Big)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\Big(\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\Big). \tag{71}$$

Equations (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 κ. If, for example, l is even, and we want to describe a state of even parity, Eqs. (70) couple the functions $f_l^{\kappa+}$ and $f_l^{\kappa-}$ for $\kappa=0, 2, 4, \cdots, l$. This involves $l/2$ pairs plus one function (for $\kappa=0$, $\mathfrak{D}_l^{0-}$ is zero, hence f_l^{0-} can be taken to be zero) or $l+1$ functions. The odd-parity equations for the same l correspond to the coupling of the function with $\kappa=1, 3, \cdots, l-1$. This relates $l/2$ pairs of l functions to each other. Both even and odd parity together therefore involve $(2l+1)$ functions corresponding to the $(2l+1)$ degeneracy of the vector spherical harmonics for a given m. For l odd, there are l functions involved in the even-parity equations and $l+1$ 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 $f_l^{\kappa\pm}(r_1, r_2, \theta_{12})$ is that they are either symmetric or antisymmetric; thus they may be confined to the region, say, $r_1\geq r_2$. If, for example, the exchange character of $f_l^{\kappa+}$ is symmetric (which, according to (52), implies that $f_l^{\kappa-}$ is antisymmetric), then these properties may be embodied in the boundary conditions[11]:

$$\Big[\frac{\partial}{\partial n}f_l^{\kappa+}(r_1, r_2, \theta_{12})\Big]_{r_1=r_2}=0, \tag{72}$$

where $\partial/\partial n$ represents the normal derivative, and

$$[f_l^{\kappa-}(r_1, r_2, \theta_{12})]_{r_1=r_2}=0, \tag{73}$$

and the solution from there on involves only the region $r_1>r_2\geq 0$. 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

$$F_l^{\kappa}(r_1, r_2, \theta_{12})\equiv f_l^{\kappa+}(r_1, r_2, \theta_{12})+f_l^{\kappa-}(r_1, r_2, \theta_{12}) \tag{74}$$

and

$$\tilde{F}_l^{\kappa}(r_1, r_2, \theta_{12})\equiv f_l^{\kappa+}(r_1, r_2, \theta_{12})-f_l^{\kappa-}(r_1, r_2, \theta_{12}), \tag{75}$$

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[11] A. Temkin, Phys. Rev. **126**, 130 (1962); P. Luke, R. Meyerott, and W. Clendenin, *ibid.* **85**, 401 (1952).

[12] A. Temkin and E. Sullivan, Phys. Rev. **129**, 1250 (1963).

then from Eq. (52)

$$\tilde{F}_l^{\kappa}(r_2, r_1, \theta_{12}) = \pm(-1)^{l+\kappa} F_l^{\kappa}(r_1, r_2, \theta_{12}) \qquad (76)$$

for singlet (upper sign) and triplet (lower sign) cases.

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

$$\Bigg[\left[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\right]F_l^{\kappa}-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\Bigg[\left(\frac{l(l+1)-\kappa^2}{2\sin^2\theta_{12}}+\frac{\kappa^2}{4}\right)F_l^{\kappa}$$
$$-\frac{\cot\theta_{12}}{4\sin\theta_{12}}l(l+1)\,\delta_{1\kappa}\tilde{F}_l^{\kappa}+\frac{\cot\theta_{12}}{4\sin\theta_{12}}B_l^{\kappa+2}$$
$$\times\{F_l^{\kappa+2}-\tfrac{1}{2}\delta_{0\kappa}(F_l^{\kappa+2}-\tilde{F}_l^{\kappa+2})\}$$
$$+\frac{\cot\theta_{12}}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa})B_{l\kappa}\{F_l^{\kappa-2}+\delta_{2\kappa}\tilde{F}_l^{\kappa-2}\}\Bigg]$$
$$+\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\Bigg[\kappa\left(\tfrac{1}{2}\cot\theta_{12}+\frac{\partial}{\partial\theta_{12}}\right)\tilde{F}_l^{\kappa}-\frac{l(l+1)}{4\sin\theta_{12}}\delta_{1\kappa}F_l^{\kappa}$$
$$+\frac{B_l^{\kappa+2}}{4\sin\theta_{12}}\{-\tilde{F}_l^{\kappa+2}+\tfrac{1}{2}\delta_{0\kappa}(F_l^{\kappa+2}+\tilde{F}_l^{\kappa+2})\}$$
$$+\frac{B_{l\kappa}}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa})\{\tilde{F}_l^{\kappa-2}+\delta_{2\kappa}F_l^{\kappa-2}\}\Bigg]=0. \qquad (77)$$

These equations, depending as they do on F_l and $\tilde{F}_l$, are more analogous to the form of 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_l^{κ} and $\tilde{F}_l^{\kappa}$ and yet there is only one equation (for a given κ). This question, in fact would appear to be particularly relevant as the previous form of our equations, (70), does constitute a coupled set for a given κ. 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_l^{κ} is the collection of numbers associated with these grid points. F_l^{κ} 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^{κ}. Now everytime an $\tilde{F}_l^{\kappa}$ 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^{κ} 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 κ whereas (77) is not is due to the fact that the functions F_l^{κ} are asymmetric and therefore must be solved for in the whole r_1, r_2, θ_{12} space. On the other hand the $f_l^{\kappa\pm}$ functions are either symmetric or antisymmetric, and therefore they are restricted to the $r_1 \geq r_2$, θ_{12} (or equivalently to the $r_1 \leq r_2$, 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^{κ} and $\tilde{F}_l^{\kappa}$ 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^{κ}, one need only interchange r_1 and r_2 in the expression to obtain $\tilde{F}_l^{\kappa}$.

It should be emphasized that the form of these equations is different from that of Breit.[2] Nevertheless the two forms must be equivalent. This is shown explicitly for the P-wave equation in Appendix III.

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,

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

so that V commutes with the angular momentum and therefore appears as an additional diagonal term in the radial equations. The interparticle 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 points. 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 $\cos\theta_{12}$.[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[13–15]

[13] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).
[14] C. Schwartz, Phys. Rev. **126**, 1015 (1962).
[15] A. W. Weiss and J. B. Martin, Phys. Rev. **132**, 2119 (1963). For a somewhat different finding from those of Refs. 13 and 14 and the preceding paper of this reference, cf. W. Lakin, Atomic Energy Commission Report NYO-10, 430, 1963 (unpublished).

principally because such a relative partial-wave expansion necessarily converges slowly where the electron-electron interaction is large (r_{12} small). The argument has some validity 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 elsewhere.[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.

$$\begin{aligned}
&\left[L_{r_{12}}+\frac{2m}{\hbar^2}(E-V)\right]F_l^{\kappa}-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\\
&\quad\times\Bigg[\left\{[l(l+1)-\kappa^2]\frac{2r_1^2r_2^2}{\rho^2}+\frac{\kappa^2}{4}\right\}F_l^{\kappa}\\
&\quad-l(l+1)\,\delta_{1\kappa}(r_1^2+r_2^2-r_{12}^2)\frac{r_1r_2}{2\rho^2}\tilde{F}_l^{\kappa}\\
&\quad+B_l^{\kappa+2}(r_1^2+r_2^2-r_{12}^2)\frac{r_1r_2}{2\rho^2}\{F_l^{\kappa+2}-\tfrac{1}{2}\delta_{0\kappa}(F_l^{\kappa+2}-\tilde{F}_l^{\kappa+2})\}\\
&\quad+B_{l\kappa}(1-\delta_{0\kappa}-\delta_{1\kappa})(r_1^2+r_2^2-r_{12}^2)\frac{r_1r_2}{2\rho^2}\\
&\quad\times\{F_l^{\kappa-2}+\delta_{2\kappa}\tilde{F}_l^{\kappa-2}\}\Bigg]+\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\\
&\quad\times\Bigg[\frac{\kappa}{2}\left\{\frac{r_1^2+r_2^2-r_{12}^2}{\rho}+\frac{\rho}{r_{12}}\frac{\partial}{\partial r_{12}}\right\}\tilde{F}_l^{\kappa}+B_l^{\kappa+2}\frac{r_1r_2}{2\rho}\\
&\quad\times\{-\tilde{F}_l^{\kappa+2}+\tfrac{1}{2}\delta_{0\kappa}(F_l^{\kappa+2}+\tilde{F}_l^{\kappa+2})\}-\delta_{1\kappa}l(l+1)\frac{r_1r_2}{2\rho}F_l^{\kappa}\\
&\quad+B_{l\kappa}\cdot\frac{r_1r_2}{2\rho}(1-\delta_{0\kappa}-\delta_{1\kappa})\{\tilde{F}_l^{\kappa-2}+\delta_{2\kappa}F_l^{\kappa-2}\}\Bigg]=0.
\end{aligned}\tag{79}$$

Here,

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

The quantity whose square root ρ is can easily be shown to be positive definite. In the equation (79) the F_l^{κ} is understood to be a function of r_1, r_2, r_{12}:

$$F_l^{\kappa}=F_l^{\kappa}(r_1,r_2,r_{12}).$$

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}:

$$\begin{aligned}
L_{r_{12}}=&\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2+\frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12}+\frac{r_1^2+r_{12}^2-r_2^2}{r_1r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}\\
&+\frac{r_2^2+r_{12}^2-r_1^2}{r_2r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}.
\end{aligned}\tag{81}$$

The equations (79) can readily be put in the form of coupled equations for a given κ.

One salient feature of the various forms of the present equations is that they are manifestly real, whereas one term in the earlier treatments of Holmberg and Diehl *et al.* is imaginary.[6] It is clear that the radial 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 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

[16] A. Temkin, Phys. Rev. Letters **6**, 354 (1961).
[17] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[18] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959). C. Schwartz, *ibid.* **128**, 1146 (1962).

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:

$$\lim_{r_1\to\infty} \Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2) = (1/r_1) \sin (kr_1+\delta_l-\tfrac{1}{2}l\pi)\, Y_{l0}(\Omega_1) \times [R_{1s}(r_2)/r_2] Y_{00}(\Omega_2), \quad (82)$$

where $[R_{1s}(r_2)/r_2]Y_{00}(\Omega_2)$ is the ground state of the one-electron atom (hydrogen). On the other hand, from Eq. (51)

$$\lim_{r_1\to\infty} \Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_1} \sin \left(kr_1+\delta_l - l\frac{\pi}{2}\right) \frac{R_{s}(r_2)}{r_2} \cdot \sum_{\kappa}{}'' [\alpha_l^{\kappa+}(\theta_{12}) \mathfrak{D}_l^{\kappa+}(\Theta, \Phi, \Psi) + \alpha_l^{\kappa-}(\theta_{12}) \mathfrak{D}_l^{\kappa-}(\Theta, \Phi, \Psi)], \quad (83)$$

where

$$\alpha_l^{\kappa\pm}(\theta_{12}) = Y_{00} \int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} \mathfrak{D}_l^{\kappa\pm}(\Theta, \Phi, \Psi)\, Y_{l0}(\vartheta_1) \times \sin \Theta\, d\Theta\, d\Phi\, d\Psi. \quad (84)$$

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

The quadrature in (84) can readily be performed by recalling from Sec. 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_l (cos ϑ_1) via the addition theorem for spherical harmonics. In its real form[9] this gives in the present case

$$P_l(\vartheta_1) = P_l(\pi/2) P_l(\Theta) + 2\sum_{m=1}^{l} (-1)^m \frac{(l-m)!}{(l+m)!} \times P_l^m(\pi/2) P_l^m(\Theta) \cos m(\Psi - \tfrac{1}{2}\theta_{12}). \quad (85)$$

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

$$d_l^{0,\kappa}(\Theta) = [(l-\kappa)!/(l+\kappa)!]^{\frac{1}{2}} P_l^{\kappa}(\Theta). \quad (86)$$

Substitution into (84) now yields the desired result:

$$\alpha_l^{\kappa+}(\theta_{12}) = P_l^{\kappa}\left(\frac{\pi}{2}\right) \left[\frac{(l-\kappa)!}{(l+\kappa)!}\right]^{\frac{1}{2}} \left\{\frac{\delta_{0\kappa}}{\sqrt{2}} + (1-\delta_{0\kappa}) \cos\left(\kappa \frac{\theta_{12}}{2}\right)\right\}, \quad (87a)$$

$$\alpha_l^{\kappa-}(\theta_{12}) = P_l^{\kappa}(\pi/2) [(l-\kappa)!/(l+\kappa)!]^{\frac{1}{2}} \sin (\kappa\theta_{12}/2). \quad (87b)$$

The radial functions themselves thus approach

$$\lim_{r_1\to\infty} f_l^{\kappa\pm}(r_1, r_2, \theta_{12}) = \frac{1}{r_1} \sin \left(kr_1+\delta_l - \frac{l\pi}{2}\right) \frac{R_{1s}(r_2)}{r_2} \alpha_l^{\kappa\pm}(\theta_{12}) \quad (88)$$

in which form we see that the r_1, r_2 dependence of all the limiting forms of the $f_l^{\kappa\pm}$ functions is independent of κ, 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 behavior is strictly the r_1, r_2 dependence in (88). (Cf. Appendix III.)

For bound-state problems, it is clear that all the radial functions 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 to pi mesic atoms, although as the mass of the identical particles get 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 conditions like (72) must be changed to matching conditions of the asymmetric 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.

A major further application of this approach is to two-electron diatomic molecules. In this case, the extension from one[20] to two electrons is non-trivial. However, the analysis has been completed and will be published elsewhere.[21]

[19] A. Temkin, Proc. Phys. Soc. (London) **80**, 1277 (1962).
[20] A. Temkin, J. Chem. Phys. **39**, 161 (1963).
[21] A. Temkin and A. K. Bhatia (to be published). The derivation of the radial equations with these Euler angles for two identical particles and a third particle of finite mass has now been completed and is being prepared for publication.

APPENDIX I

In this appendix, we prove the Eqs. (65) and (66). For $m=0$, $\partial/\partial\Phi$ terms give zero. Therefore, we can write

$$\Lambda_1 \to \frac{\partial^2}{\partial\Theta^2} - \cot\Theta\frac{\partial}{\partial\Theta} - \cot^2\Theta\frac{\partial^2}{\partial\Psi^2}, \tag{I1}$$

$$\Lambda_2 \to 2\cot\Theta\frac{\partial^2}{\partial\Psi\partial\Theta} - \frac{\partial}{\partial\Psi} - 2\cot^2\Theta\frac{\partial}{\partial\Psi}. \tag{I2}$$

We also write (for $\mu>0$)

$$\mathfrak{D}_l^{\kappa+} = N_{l\kappa}\cos\kappa\Psi\sin^\kappa\Theta F_\kappa, \tag{I3}$$

$$\mathfrak{D}_l^{\kappa-} = N_{l\kappa}\sin\kappa\Psi\sin^\kappa\Theta F_\kappa, \tag{I4}$$

where

$$N_{l\kappa} = \frac{(-1)^\kappa}{2^\kappa\cdot\kappa!}\left[\frac{2l+1}{4\pi^2}\frac{(l+\kappa)!}{(l-\kappa)!}\right]^{\frac{1}{2}} \tag{I5}$$

and

$$F_\kappa = F(\kappa-l, \kappa+l+1; 1+\kappa; \sin^2(\Theta/2)). \tag{I6}$$

Now

$$\Lambda_1\mathfrak{D}_l^{\kappa+} = N_{l\kappa}\cos\kappa\Psi[2\kappa(\kappa-1)\sin^{\kappa-2}\Theta\cos^2\Theta F_\kappa - \kappa\sin^\kappa\Theta F_\kappa + 2\kappa\sin^\kappa\Theta\cos\Theta A_{l\kappa}F_{\kappa+1} + \sin^{\kappa+2}\Theta A_{l\kappa}A_{l,\kappa+1}F_{n+2}], \tag{I7}$$

where we have used the well-known relations for the derivatives of hypergeometric functions:

$$\frac{d}{d\Theta}F_\kappa = A_{l\kappa}\sin\Theta F_{\kappa+1} \tag{I8}$$

$$\frac{d^2}{d\Theta^2}F_\kappa = A_{l\kappa}\cos\Theta F_{\kappa+1} + A_{l\kappa}A_{l,\kappa+1}\sin^2\Theta F_{\kappa+2}. \tag{I9}$$

A relation between F_κ, $F_{\kappa+1}$, and $F_{\kappa+2}$ can be obtained from the differential equation satisfied by the hypergeometric function

$$\cos\Theta F_{\kappa+1} = F_\kappa - \sin^2\Theta\frac{A_{l,\kappa+1}}{2(1+\kappa)}\cdot F_{\kappa+2}. \tag{I10}$$

Using (I10) in (I7), we find

$$\Lambda_1\mathfrak{D}_l^{\kappa+} = N_{l\kappa}\cos\kappa\Psi[2\kappa(\kappa-1)\sin^{\kappa-2}\Theta\cos^2\Theta F_\kappa - \kappa\sin^\kappa\Theta F_\kappa + 2\kappa\sin^\kappa\Theta A_{l\kappa}F_\kappa + (1/1+\kappa)\sin^{\kappa+2}\Theta A_{l\kappa}A_{l,\kappa+1}F_{\kappa+2}]. \tag{I11}$$

Similarly,

$$\Lambda_2\mathfrak{D}_l^{\kappa+} = -N_{l\kappa}\sin\kappa\Psi\left[2\kappa(\kappa-1)\sin^{\kappa-2}\Theta\cos^2\Theta F_\kappa - \kappa\sin^\kappa\Theta F_\kappa + 2\kappa\sin^\kappa\Theta A_{l\kappa}F_\kappa - \frac{\kappa}{\kappa+1}\sin^{\kappa+2}\Theta A_{l\kappa}A_{l,\kappa+1}F_{\kappa+2}\right]. \tag{I12}$$

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

$$(\sin 2\Psi\Lambda_2 - \cos 2\Psi\Lambda_1)\mathfrak{D}_l^{\kappa+} = -N_{l\kappa}\cos(\kappa-2)\Psi\cdot G - \tfrac{1}{2}(N_{l\kappa}/N_{l,\kappa+2})A_{l\kappa}A_{l,\kappa+1}\mathfrak{D}_l^{(\kappa+2)+}, \tag{I13}$$

where

$$G = [2\kappa(\kappa-1)\sin^{\kappa-2}\Theta\cos^2\Theta - \kappa\sin^\kappa\Theta + 2\kappa A_{l\kappa}\sin^\kappa\Theta]F_\kappa + [(1-\kappa)/2(1+\kappa)]\sin^{\kappa+2}\Theta A_{l\kappa}A_{l,\kappa+1}F_{\kappa+2}. \tag{I14}$$

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

$$\cos\Theta F_{\kappa+2} = F_{\kappa+1} - \sin^2\Theta\frac{A_{l,\kappa+2}}{2(\kappa+2)}F_{\kappa+3}.$$

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

$$\left[\cos^2\Theta\left(\frac{\kappa+2}{\kappa+1}\right) + \frac{\kappa+2}{2(\kappa+1)^2}\sin^2\Theta A_{l,\kappa+1} + \sin^2\Theta\frac{A_{l,\kappa+2}}{2(\kappa+1)}\right] \times F_{\kappa+2} - \sin^4\Theta\frac{A_{l,\kappa+2}A_{l,\kappa+3}}{4(\kappa+1)(\kappa+3)}F_{\kappa+4} = \left(\frac{\kappa+2}{\kappa+1}\right)F_\kappa.$$

Letting $\kappa\to\kappa-2$ multiplying by $2(\kappa-1)^2\sin^{\kappa-2}\Theta$ and rearranging, we have for $\kappa\geq 2$

$$G = 2\kappa(\kappa-1)\sin^{\kappa-2}\Theta\cdot F_{\kappa-2}. \tag{I15}$$

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

$$G = \tfrac{1}{2}\sin^2\Theta A_{l0}A_{l1}F_2, \qquad \kappa=0; \tag{I16}$$

$$G = -\frac{l(l+1)}{2}\sin\Theta F_1, \qquad \kappa=1. \tag{I17}$$

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

$$2(\sin 2\Psi\Lambda_2 - \cos 2\Psi\Lambda_1)\mathfrak{D}_l^{\kappa+} = -B_l^\kappa\mathfrak{D}_l^{(\kappa-2)+} - B_{l,\kappa+2}\mathfrak{D}_l^{(\kappa+2)+}, \tag{I18}$$

where B_l^κ has already been defined in Eq. (68b).

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

$$2(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)\mathfrak{D}_l^{0+}=-\sqrt{2}B_{l2}\mathfrak{D}_l^{2+} \quad \text{(I19)}$$

and

$$2(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)\mathfrak{D}_l^{1+}=l(l+1)\mathfrak{D}_l^{1+}-B_{l3}\mathfrak{D}_l^{3+}. \quad \text{(I20)}$$

We can combine (I18, I19, I20) to get Eq. (65a). Similarly, we can prove (65b), (66a), (66b).

APPENDIX II

We can form the raising and lowering operators $M_\pm=M_x\pm iM_y$ by using Eqs. (36) and (37). It can be proved including phase factors that

$$(i/\hbar)M_+\mathfrak{D}_l^{m,k}=-[(l-m)(l+m+1)]^{\frac{1}{2}}\mathfrak{D}_l^{m+1,k}, \quad \text{(II1)}$$

$$(i/\hbar)M_-\mathfrak{D}_l^{m,k}=[(l+m)(l-m+1)]^{\frac{1}{2}}\mathfrak{D}_l^{m-1,k}. \quad \text{(II2)}$$

It is well-known that $M_\pm$ commutes with H, and in particular with the kinetic energy. One can show explicitly that they commute with the relevant part of the kinetic energy given below:

$$[\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1, M_\pm]=0, \quad \text{(II3)}$$

$$[\sin 2\Psi\Lambda_1+\cos 2\Psi\Lambda_2, M_\pm]=0. \quad \text{(II4)}$$

It may be useful to give the following relations

$$[\Lambda_1, M_\pm]=\pm(2\hbar/\sin\Theta)\exp(\pm i\Phi)\Lambda_2, \quad \text{(II5)}$$

$$[\Lambda_2, M_\pm]=\mp(2\hbar/\sin\Theta)\exp(\pm i\Phi)\Lambda_1. \quad \text{(II6)}$$

Below we give the results of the raising and lowering operators on the exchange vector spherical harmonics. These results may be derived from Eqs. (II1), (II2) and the definition (54).

$$(i/\hbar)M_+\mathfrak{D}_l^{(m,\kappa)\pm}=-[(l-m)(l+m+1)]^{\frac{1}{2}}\mathfrak{D}_l^{(m+1,\kappa)\pm}, \quad \text{(II7)}$$

$$(i/\hbar)M_-\mathfrak{D}_l^{(m,\kappa)\pm}=[(l+m)(l-m+1)]^{\frac{1}{2}}\mathfrak{D}_l^{(m-1,\kappa)\pm}. \quad \text{(II8)}$$

Operating $M_\pm$ on Eqs. (65a), we find

$$\begin{aligned}M_+2(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)\mathfrak{D}_l^{\kappa+}&=-B_l^\kappa(1-\delta_{0\kappa}-\delta_{1\kappa})M_+\mathfrak{D}_l^{(\kappa-2)+}+\delta_{1\kappa}l(l+1)M_+\mathfrak{D}_l^{\kappa+}\\&\quad-(1+\delta_{0\kappa})B_{l,\kappa+2}M_+\mathfrak{D}_l^{(\kappa+2)+}. \quad \text{(II9)}\end{aligned}$$

Using Eqs. (II3) and (II7), we get

$$\begin{aligned}2(\sin 2\Psi\Lambda_2-\cos 2\Psi\Lambda_1)\mathfrak{D}_l^{(1,\kappa)+}&=-B_l^\kappa(1-\delta_{0\kappa}-\delta_{1\kappa})\mathfrak{D}_l^{(1,\kappa-2)+}+\delta_{1\kappa}l(l+1)\mathfrak{D}_l^{(1,\kappa)+}\\&\quad-(1+\delta_{0\kappa})B_{l,\kappa+2}\mathfrak{D}_l^{(1,\kappa+2)+}. \quad \text{(II10)}\end{aligned}$$

With repeated operation of M_+, it follows by induction that the above relation is true for any m. Similarly we can obtain Eqs. (65b), (66a) and (66b) for any m. Thus the radial equations are independent of m.

It can also be shown that

$$\Psi_{l-m}=(-1)^m\Psi_{lm}^*. \quad \text{(II11)}$$

In order to show this it is only necessary to state the easily derivable relation

$$[\mathfrak{D}_l^{(m,\kappa)\pm}]^*=(-1)^m\mathfrak{D}_l^{(-m,\kappa)\pm}. \quad \text{(II12)}$$

APPENDIX III

It can be seen very easily that the P-wave even-parity equations are the same as that of Breit. For odd parity, we show here that our radial equations are equivalent to Breit's.

The relation between Hylleraas–Breit Euler angles (denoted by a subscript B) and our angles can easily be shown to be

$$\sin\Theta_B\cos\Psi_B=\sin\Theta\sin(\Psi-\tfrac{1}{2}\theta_{12}), \quad \text{(III1)}$$

$$\cos\Theta_B=-\sin\Theta\cos(\Psi-\tfrac{1}{2}\theta_{12}). \quad \text{(III2)}$$

For the symmetric, odd-parity case, Breit's wave function[2,3] is

$$\begin{aligned}\Psi&=\cos\Theta_B[f(r_1,r_2,\theta_{12})+\cos\theta_{12}f(r_2,r_1,\theta_{12})]\\&\quad+\sin\Theta_B\cos\Psi_B\sin\theta_{12}f(r_2,r_1,\theta_{12})\\&=-\sin\Theta\cos\Psi\cos\tfrac{1}{2}\theta_{12}(f+\tilde{f})\\&\quad-\sin\Theta\sin\Psi\sin\tfrac{1}{2}\theta_{12}(f-\tilde{f}), \quad \text{(III3)}\end{aligned}$$

where

$$f=f(r_1,r_2,\theta_{12}),$$

$$\tilde{f}=f(r_2,r_1,\theta_{12}).$$

Comparing (III3) with Eq. (51), we find that our radial functions $f_1^{1\pm}$ are related to Breit's f and $\tilde{f}$ by

$$f_1^{1+}=-\cos\tfrac{1}{2}\theta_{12}(f+\tilde{f}), \quad \text{(III4)}$$

$$f_1^{1-}=-\sin\tfrac{1}{2}\theta_{12}(f-\tilde{f}). \quad \text{(III5)}$$

Substituting (III4) in Eq. (70a) for $l=1$, $\kappa=1$, yield

$$\begin{aligned}&\left[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\right](f+\tilde{f})-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\\&\times\left[\tfrac{1}{2}\cot\theta_{12}\tan\frac{\theta_{12}}{2}+\frac{1}{2}+\frac{1}{2\sin^2\theta_{12}}-\frac{\cot\theta_{12}}{2\sin\theta_{12}}\right](f+\tilde{f})\\&-\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\left[\tfrac{1}{2}\cot\theta_{12}\tan\frac{\theta_{12}}{2}+\frac{1}{2}+\frac{1}{2\sin\theta_{12}}\tan\frac{\theta_{12}}{2}\right]\\&\times(f-\tilde{f})-2\tan\frac{\theta_{12}}{2}\left[\frac{1}{r_1^2}\frac{\partial f}{\partial\theta_{12}}+\frac{1}{r_2^2}\frac{\partial\tilde{f}}{\partial\theta_{12}}\right]=0. \quad \text{(III6)}\end{aligned}$$

Similarly substitution of (III5) in Eq. (70b) for $l=1$, $\kappa=1$ gives

$$\left[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\right](f-\tilde{f})+\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)$$
$$\times\left[\tfrac{1}{2}\cot\theta_{12}\cot\frac{\theta_{12}}{2}-\frac{1}{2}-\frac{1}{2\sin^2\theta_{12}}-\frac{\cot\theta_{12}}{2\sin\theta_{12}}\right](f-\tilde{f})$$
$$+\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\left[-\frac{1}{2}+\tfrac{1}{2}\cot\theta_{12}\cot\frac{\theta_{12}}{2}-\frac{\cot\frac{1}{2}\theta_{12}}{2\sin\theta_{12}}\right](f+\tilde{f})$$
$$+2\cot\frac{\theta_{12}}{2}\left[\frac{1}{r_1^2}\frac{\partial f}{\partial\theta_{12}}-\frac{1}{r_2^2}\frac{\partial\tilde{f}}{\partial\theta_{12}}\right]=0. \qquad \text{(III7)}$$

Adding (III6) and (III7), we find after some simplification

$$\left[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\right]f+\frac{2}{r_1^2}\left(\cot\theta_{12}\frac{\partial f}{\partial\theta_{12}}-f\right)$$
$$-\frac{2}{r_2^2\sin\theta_{12}}\frac{\partial\tilde{f}}{\partial\theta_{12}}=0,$$

which is the same equation given by Breit.[2,3]

The equivalence of our equation with Breit's antisymmetric, odd-parity, P-wave equation may be shown in a completely analogous manner.