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SEPARATION OF ANGLES IN THE TWO-ELECTRON PROBLEM

BY G. BREIT

DEPARTMENT OF PHYSICS, NEW YORK UNIVERSITY

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ABSTRACT

Neglecting the spin, two electrons are described in quantum mechanics by means of a wave equation in six variables. It is shown that well-known relations between angular momentum operators make it possible to determine the dependence of the wave function on three variables. The problem is thus reduced from *six* to *three* dimensions. For a state with an assigned "orbital" angular momentum l, say an S, P, D state the dependence of the wave function on three Euler angles is determined by the value of l. The wave function is a linear combination of products of distance and angle functions, the latter depending only on the three Euler angles. The angle functions are well-known solutions of the wave equation for a symmetrical top. The distance functions satisfy wave equations in three variables r_1, r_2, r_{12} or r_1, r_2, θ. The case of P terms is worked out in detail. Equations (10), (25) apply to two electrons having the *same azimuthal quantum number*. Equations (18), (20), (24) describe all the other cases, for instance S and P electrons combining to give ^1P and ^3P. Triplets are described by (18) and singlets by (20).

TWO electrons are treated in quantum mechanics by means of a six dimensional wave equation. In most atomic problems it is sufficient to consider the two electrons under the influence of a central field of force and to treat all other questions by perturbation methods. It is well known that in this approximation essential simplifications are introduced by the spherical symmetry of the central field of force. The eigenfunctions may be arranged in non-combining systems, each system corresponding to a certain value of the total angular momentum. By considerations of this sort it has been shown that correct space quantization, multiplet intensity relations, selection rules, and anomalous Zeeman effect formulas are consequences of quantum mechanics.†

In the calculations of the two or many electron problem it is customary at present to employ an approximation method such as Hartree's and to

† See in particular E. Wigner, Zeits. f. Physik **43**, 624 (1927) and especially p. 640 where the general possibility of (6) below is pointed out. The difference between the present treatment and Wigner's lies in the use of (4) with its known system of eigenfunctions.

consider each electron as subject to the action of a central field of force. In the calculations of the normal energy levels of He, however, Hylleraas[1] found it useful to consider the problem exactly. His calculations apply to the S states, which reduces the problem to a three dimensional one. We shall see that the reduction from six to three dimensions can be always made and that it is an immediate consequence of the spherical symmetry of the field. Even though the solution of a three dimensional wave equation is difficult we believe to have simplified the general problem because the application of variational methods, such as the Ritz method to a six or five dimensional problem is usually out of the question.

Let ψ be the Schroedinger function. Let the coordinates of the electrons be (x_1, y_1, z_1), (x_2, y_2, z_2). By the general theorem of conservation of angular momentum

$$\left[\sum_{x,y,z,}\left(y_1\frac{\partial}{\partial z_1}-z_1\frac{\partial}{\partial y_1}+y_2\frac{\partial}{\partial z_2}-z_2\frac{\partial}{\partial y_2}\right)+l(l+1)\right]\psi=0 \qquad (1)$$

for any state with angular momentum l. Introducing polar coordinates (r_1, θ_1, ϕ_1), (r_2, θ_2, ϕ_2) this becomes

$$\left\{\left(\sin\phi_1\frac{\partial}{\partial\theta_1}+\cos\phi_1\frac{\cos\theta_1}{\sin\theta_1}\frac{\partial}{\partial\phi_1}+\sin\phi_2\frac{\partial}{\partial\theta_2}+\cos\phi_2\cot\theta_2\frac{\partial}{\partial\phi_2}\right)^2\right.$$
$$+\left(-\cos\phi_1\frac{\partial}{\partial\theta_1}+\sin\phi_1\cot\theta_1\frac{\partial}{\partial\phi_1}-\cos\phi_2\frac{\partial}{\partial\theta_2}+\sin\phi_2\cot\theta_2\frac{\partial}{\partial\phi_2}\right)^2$$
$$\left.+\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)^2+l(l+1)\right\}\psi=0. \qquad (2)$$

We now reexpress ψ in terms of Euler angles θ', ϕ',ϕ and r_1, r_2, θ connected by the transformation formulas:

$$\theta'=\theta_1,\quad \phi'=\phi_1$$
$$\cos\theta=\cos\theta'\cos\theta_2+\sin\theta'\sin\theta_2\cos(\phi_2-\phi_1);\qquad \sin\theta_2\sin\alpha=\sin\theta'\sin\phi$$
$$\cos\theta_2=\cos\theta'\cos\theta-\sin\theta'\sin\theta\cos\phi;\qquad \sin\theta\sin\alpha=\sin\theta'\sin(\phi_2-\phi_1) \qquad (3)$$
$$\cos\theta'=\cos\theta_2\cos\theta+\sin\theta_2\sin\theta\cos\alpha;\qquad \sin\theta\sin\phi=\sin\theta_2\sin(\phi_2-\phi_1)$$

the notation being throughout as in the first paper of Hylleraas. The angle θ drops out of (2) which reduces itself to

$$\left\{\frac{\partial^2}{\partial\theta'^2}+\cot\theta'\frac{\partial}{\partial\theta'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi^2}-2\frac{\cos\theta'}{\sin^2\theta'}\frac{\partial^2}{\partial\phi\partial\phi'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi'^2}+l(l+1)\right\}\psi=0. \qquad (4)$$

[1] Hylleraas, Zeits. f. Physik **54,** 347 (1929); **48,** 469 (1928). See also J. C. Slater, Proc. Nat. Acad. **13,** 423 (1927); G. W. Kellner, Zeits. f. Physik **44,** 91 (1927).

[2] For derivation see appendix I.

This is a well-known equation, being a special case of the wave equation for a symmetrical top. Its eigenwerte are known to correspond to integral values of l, the value zero being included. The angular momentum about the z axis is represented by the operator

$$M^z=\frac{h}{2\pi i}\left(x_1\frac{\partial}{\partial y_1}-y_1\frac{\partial}{\partial x_1}+x_2\frac{\partial}{\partial y_2}-y_2\frac{\partial}{\partial x_2}\right)=\frac{h}{2\pi i}\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)=\frac{h}{2\pi i}\ \frac{\partial}{\partial\phi'}. \quad (5)$$

If $l(l+1)=0$ there are no eingfunctions (4) except those which do not depend on θ', ϕ, ϕ'. Thus for $l=0$ the wave function depends only on r_1, r_2, θ or r_1, r_1, r_{12} as pointed out by Hylleraas for S states. In all other cases i.e. for P, D, states ψ depends on the angles. Thus for P states ($l=1$) we have the following nine independent eigenfunctions

$$\cos\theta',\ (1+\cos\theta')e^{\pm i(\phi+\phi')},\ e^{\pm i\phi}\sin\theta',\ e^{\pm i\phi'}\sin\theta',\ (1-\cos\theta')e^{\pm i(\phi-\phi')}.$$

We may say therefore that for any P state

$$\psi=\sum_{i=1}^{0}f_i(r_1,r_2,\theta)u_i(\theta',\phi',\phi) \quad (6)$$

where $u_1, \cdots u_0$ are the above set of nine independent eigenfunctions. Equation (6) is, however, too general because the nine eigenfunctions can be subdivided into three non-combining sets, each set containing three functions, all the functions of a given set depending on ϕ' as $e^{im\phi'}$. According to (5) each set describes such an orientation of the total angular momentum that its component along OZ is $mh/2\pi$. For $m=0$ such a set of functions is

$$\cos\theta',\ e^{\pm i\phi}\sin\theta'. \quad (6')$$

In (6) therefore, it is permissible to extend the summation only over these three functions if we are interested only in solutions with $m=0$. The legitimacy of using only these three functions is of course a consequence of the invariance of the Hamiltonian under rotations about the z axis. On account of this invariance the result of operating by the Hamiltonian on any term in (6) gives rise to angular functions with the same value of m. In the general expression (6) therefore each set of functions is entirely independent of the other two.

Since the two electrons are equal we have a further subdivision into non-combining term systems. This is the usual subdivision into symmetric and antisymmetric solutions. With this in mind we use Hylleraas' expressions (23), (24) according to which the Schroedinger equation for the energy is

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial\psi}{\partial r_1}\right)+\frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial\psi}{\partial r_2}\right)+\frac{1}{r_1^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+A_1[\psi]\right]$$
$$+\frac{1}{r_2^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+A_2[\psi]\right]+8\pi^2mh^{-2}(E-V)\psi=0$$

$$A_1[\psi]=(\cot^2\theta+2\cot\theta\cot\theta'\cos\phi+\cot^2\theta')\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{\sin\theta'}\frac{\partial}{\partial\theta'}\left(\sin\theta'\frac{\partial\psi}{\partial\theta'}\right)$$
$$+\frac{1}{\sin^2\theta'}\frac{\partial^2\psi}{\partial\phi'^2}+2\cot\theta'\sin\phi\frac{\partial^2\psi}{\partial\theta\partial\phi}-2\cos\phi\frac{\partial^2\psi}{\partial\theta\partial\theta'}-2\frac{\sin\phi}{\sin\theta'}\frac{\partial^2\psi}{\partial\theta\partial\phi'}$$
$$+2\cot\theta\sin\phi\frac{\partial^2\psi}{\partial\phi\partial\theta'}-\frac{2}{\sin\theta'}(\cot\theta'+\cot\theta\cos\phi)\frac{\partial^2\psi}{\partial\phi\partial\phi'};\quad A_2[\psi]=\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \tag{7}$$

On account of spherical symmetry V is a function of r_1, r_2, θ only and does not contain θ', ϕ', ϕ. The functions u_i behave therefore as constant coefficients with the exceptions of the terms $A_1[\psi]$, $A_2[\psi]$. Since by (3) $\sin\theta'\sin\phi=\sin\theta_2\sin\alpha$, the angular eigenfunction $\sin\theta'\sin\phi$ is seen to be antisymmetric in the electrons 1 and 2. For this reason A_1 and A_2 must produce similar effects on it. In fact it is found that

$$A_1[\sin\theta'\sin\phi]=A_2[\sin\theta'\sin\phi]=-\sin^{-2}\theta(\sin\theta'\sin\phi). \tag{8}$$

We see therefore that the particular linear combination of two of the eigenfunctions for $m=0$, namely $\sin\theta'\cdot\sin\phi$ when operated on by the Hamiltonian gives rise to itself only. A possible P state is therefore given by

$$\psi=f(r_1,r_2,\theta)\sin\theta'\sin\phi \tag{9}$$

and the differential equation for f is

$$\frac{\partial}{r_1^2\partial r_1}\left(r_1^2\frac{\partial f}{\partial r_1}\right)+\frac{\partial}{r_2^2\partial r_2}\left(r_2^2\frac{\partial f}{\partial r_2}\right)+(r_1^{-2}+r_2^{-2})\left[\frac{\partial}{\sin\theta\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)-\frac{f}{\sin^2\theta}\right]$$
$$+8\pi^2mh^{-2}(E-V)f=0. \tag{10}$$

This differential equation differs from the one for S states only by the term $-(r_1^{-2}+r_2^{-2})\sin^{-2}\theta$ and it is seen that the determination of its eigenvalues can be carried out by analogous methods. The physical interpretation of the solutions (9) becomes apparent if the perturbation e^2/r_{12} between the two electrons is supposed small. Then (10) is separable. Supposing the separation to take place by

$$f=P_n^{(1)}(\cos\theta)g(r_1,r_2) \tag{10'}$$

we obtain

$$\frac{\partial}{r_1^2\partial r_1}\left(r_1^2\frac{\partial f}{\partial r_1}\right)+\frac{\partial}{r_2^2\partial r_2}\left(r_2^2\frac{\partial f}{\partial r_2}\right)-n(n+1)(r_1^{-2}+r_2^{-2})f+8\pi^2mh^{-2}(E-V)f=0.$$

This may be considered as the radial part of the Schroedinger equation for two electrons, each being initially in a state with azimuthal quantum number n. The same may be seen from (10′) because by (3)

$$\sin\theta\sin\theta'\sin\phi=\sin\theta_1\sin\theta_2\sin(\phi_2-\phi_1)$$

so that the angular part of (10′) is a linear combination of products of the type $P_n{}^1(\cos\theta_1)\, e^{\pm i\phi_1}$. The solution (9) represents therefore P states which arise either from two ^2P or two ^2D or two ^2F electrons etc. The solutions of (10) may be symmetric or antisymmetric in r_1, r_2 giving the singlet and triplet systems. They include the case of equivalent orbits.

Out of the three functions (6′) we have left now only two

$$\cos\theta',\ \sin\theta'\cos\phi$$

substituting these into (7) it is found that the Hamiltonian operating on one of them gives rise not only to itself but also to the other. Here we must write

$$\psi = f_1\cos\theta' + f_2\sin\theta'\cos\phi. \tag{11}$$

Operating on this by (7) we get two simultaneous linear equations in f_1 and f_2:

$$\begin{aligned} &L[f_1] - 2r_1^{-2}\left(f_1 + \cot\theta f_2 + \frac{\partial f_2}{\partial\theta}\right) = 0 \\ &L[f_2] + r_1^{-2}\left(2\frac{\partial f_1}{\partial\theta} - \sin^{-2}\theta f_2\right) - r_2^{-2}\sin^{-2}\theta f_2 = 0 \end{aligned} \tag{12}$$

where

$$L[f] = \frac{\partial}{r_1^2\partial r_1}\left(r_1^2\frac{\partial f}{\partial r_1}\right) + \frac{\partial}{r_2^2\partial r_2}\left(r_2^2\frac{\partial f}{\partial r_2}\right) + (r_1^{-2}+r_2^{-2})\frac{\partial}{\sin\theta\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + 8\pi^2 m h^{-2}(E-V)f. \tag{13}$$

Equations (11), (12) are unsymmetrical in (1) and (2). Making the substitutions

$$F_1 = f_1 + \cot\theta\cdot f_2,\quad F_2 = (\sin\theta)^{-1} f_2 \tag{14}$$

we have

$$\psi = F_1\cos\theta_1 - F_2\cos\theta_2 \tag{15}$$

while (12) goes into[3]

$$\begin{aligned} &L[F_1] + \frac{2}{r_1^2}\left(\cot\theta\frac{\partial F_1}{\partial\theta} - F_1\right) + \frac{2\partial F_2}{r_2^2\sin\theta\partial\theta} = 0 \\ &L[F_2] + \frac{2\partial F_1}{r_1^2\sin\theta\partial\theta} + \frac{2}{r_2^2}\left(\cot\theta\frac{\partial F_2}{\partial\theta} - F_2\right) = 0. \end{aligned} \tag{16}$$

Here F_1, F_2 are functions of r_1, r_2, θ only. Any ψ in (15) must be either symmetric or antisymmetric in (1) and (2). The latter case is obtained if

$$F_2(r_1,r_2,\theta) = F_1(r_2,r_1,\theta) \equiv \tilde{F}(r_1,r_2,\theta). \tag{17}$$

[3] For direct derivation see Appendix II.

Letting $F=F_1$ the two equations (16) reduce to a single equation in F *vis.*

$$L[F]+\frac{2}{r_1^2}\left(\cot\theta\frac{\partial F}{\partial\theta}-F\right)+\frac{2}{r_2^2\sin\theta}\frac{\partial\tilde{F}}{\partial\theta}=0. \tag{18}$$

The symmetric solutions are obtained by letting

$$F_2=-\tilde{F}_1. \tag{19}$$

Here we write $F_1=G$ and (16) reduces again to a single equation

$$L[G]+\frac{2}{r_1^2}\left(\cot\theta\frac{\partial G}{\partial\theta}-G\right)-\frac{2}{r_2^2\sin\theta}\frac{\partial\tilde{G}}{\partial\theta}=0. \tag{20}$$

The only difference between (18) and (20) is in the sign of the last term. This term represents the resonance between the two electrons. In the unperturbed state i.e. if the perturbation term e^2/r_{12} is not important the simplest solutions of (18) are those for which $(\partial F/\partial\theta)=0$. Then (15) shows that we deal with a ^3P term arising from a ^2S and a ^2P electron while similarly the solutions of (20) give the corresponding ^1P terms. In addition to these solutions there are others for the unperturbed case. Thus if we set

$$F=g(r_1,r_2)\cos\theta+\tilde{g}/3$$

we find from (15) that

$$\psi=g(\cos\theta\cos\theta_1-\cos\theta_2/3)-\tilde{g}(\cos\theta\cos\theta_2-\cos\theta_1/3).$$

Since

$$\cos\theta\cos\theta_1-\cos\theta_2/3=\tfrac{2}{3}\cos\theta_2P_2(\cos\theta_1)-\cos\theta_1\sin\theta_1\sin\theta_2\cos(\phi_2-\phi_1)$$

this angular function is seen to consist of a linear combination of

$$e^{\pm im\phi_1}P_2{}^m(\cos\theta_1)\quad\text{and}\quad e^{\pm im\phi_2}P_1{}^m(\cos\theta_2).$$

This is a case of ^2P and ^2D terms combining to give a ^3P. In a similar way all other combinations between electrons of unequal azimuthal quantum number resulting in P terms are contained among the solutions of (18).

Summarizing the classifications of all solutions belonging to the subset (6′) we may say that (9) and (10) give the P terms arising from electrons which in the unperturbed state have equal azimuthal quantum numbers while (15), (18), (20) give the P terms arising from all other electron combinations.

It will be remembered now that equation (6) contains two more non-combining sets of eigenfunctions corresponding to $m=\pm 1$. The spherical symmetry of the problem enables us to write them down by analogy with those already found. Thus corresponding to (15) and (18) we have now a complete set of orthogonal eigenfunctions

$$\begin{aligned}
u_1 &= (3^{1/2}/4\pi)(F\sin\theta_1 e^{i\phi_1} - \tilde{F}\sin\theta_2 e^{i\phi_2})\\
&= (3^{1/2}/4\pi)\left[a\sin\theta' + b(-i\sin\phi - \cos\theta'\cos\phi)\right]e^{i\phi'}\\
u_0 &= (6^{1/2}/4\pi)(F\cos\theta_1 - \tilde{F}\cos\theta_2) = (6^{1/2}/4\pi)\left[a\cos\theta' + b\sin\theta'\cos\phi\right] \quad (21)\\
u_{-1} &= (3^{1/2}/4\pi)(F\sin\theta_1 e^{-i\phi_1} - \tilde{F}\sin\theta_2 e^{-i\phi_2})\\
&= (3^{1/2}/4\pi)\left[a\sin\theta' + b(i\sin\phi - \cos\theta'\cos\phi)\right]e^{-i\phi'}\\
a &= F - \tilde{F}\cos\theta, \quad b = \tilde{F}\sin\theta.
\end{aligned}$$

The normalization being such that

$$\int (F^2 - 2F\tilde{F}\cos\theta + \tilde{F}^2)dV_{r_1,r_2,\theta} = 1; \; dV_{r_1,r_2,\theta} = r_1^2 r_2^2 \sin\theta dr_1 dr_2 d\theta.$$

These three eigenfunctions belong to the eigenwerte of (18) and are to be used together in solving perturbation problems such as fine structure calculations. Similarly there are three other eigenfunctions for every solution of (20). The remaining three functions are of the type (9). We note that $\sin\theta\sin\phi = R_z/R$ where $R_z = [\vec{r}_1 \times \vec{r}_2]$. Forming the combinations $R_x \pm iR_y$ we find this set of functions to be

$$\begin{gathered}
\left[(3^{1/2}/4\pi)e^{i\phi'}(i\cos\phi - \cos\theta'\sin\phi), \quad (6^{1/2}/4\pi)\sin\theta'\sin\phi,\right.\\
\left.(3^{1/2}/4\pi)e^{-i\phi'}(-i\cos\phi - \cos\theta'\sin\phi)\right]f.
\end{gathered} \qquad (22)$$

The differential equations (16), (18) and the corresponding sets of eigenfunctions (21), (22) correspond to essentially different cases and for this reason the variational equations belonging to the two cases are different. We consider the type of solution described by (16) and (21) first. The variational equation belonging to the problem is

$$\delta\int\left\{\left(\frac{\partial\psi}{\partial x_1}\right)^2 + \cdots + \left(\frac{\partial\psi}{\partial z_2}\right)^2 + 8\pi^2 m h^{-2}(V-E)\psi^2\right\}dx_1\cdots dz_2 = 0 \qquad (23)$$

with the equation of condition

$$\int \psi^2 dx_1 \cdots dz_2 = 1. \qquad (23')$$

Here $dx_1 \cdots dz_2$ is the volume element of the six dimensional configuration space. Taking any of the functions (21) the volume element may be reexpressed in terms of r_1, r_2, θ, θ', ϕ', ϕ and the integrations may then be performed over the angles θ', ϕ', ϕ in (23) and (23′).

The result of the calculation is:[4]

$$\begin{aligned}
\delta\int &\left\{\left(\frac{\partial F_1}{\partial r_1}\right)^2 - 2\cos\theta\frac{\partial F_1}{\partial r_1}\frac{\partial F_2}{\partial r_1} + \left(\frac{\partial F_2}{\partial r_1}\right)^2 + \left(\frac{\partial F_1}{\partial r_2}\right)^2 - 2\cos\theta\frac{\partial F_1}{\partial r_2}\frac{\partial F_2}{\partial r_2} + \left(\frac{\partial F_2}{\partial r_2}\right)^2\right.\\
&+ (r_1^{-2} + r_2^{-2})\left[\left(\frac{\partial F_1}{\partial\theta}\right)^2 - 2\cos\theta\frac{\partial F_1}{\partial\theta}\frac{\partial F_2}{\partial\theta} + \left(\frac{\partial F_2}{\partial\theta}\right)^2\right] + 2r_1^{-2}F_1^2 + 2r_2^{-2}F_2^2
\end{aligned}$$

[4] For derivation see appendix II.

$$+2r_1^{-2}\sin\theta F_1\frac{\partial F_2}{\partial\theta}+2r_2^{-2}\sin\theta F_2\frac{\partial F_1}{\partial\theta}$$

$$+8\pi^2 mh^{-2}(V-E)(F_1^2-2F_1F_2\cos\theta+F^2{}_2\}\,dV_{r_1r_2\theta}=0 \tag{24}$$

and the equation of condition is

$$\int(F_1^2-2F_1F_2\cos\theta+F_2^2)dV_{r_1,r_2,\theta}=1. \tag{24'}$$

Performing independent variations of F_1 and F_2 the differential equations (16) follow from (24). Corresponding to (17) and (18) the variational equation (24) gives two different equations, one applying to an antisymmetric ψ and the other to the symmetric one. Each of these involves only one function and its transposed and can be worked out by the same method as used by Hylleraas. It will be noted that the antisymmetric solutions (24) involve combinations of the type $F^2-2F\bar{F}\cos\theta+\bar{F}^2$. If $r_1=r_2$, this vanishes for $\theta=0$, so that the values of $F(r, r, \theta)$ are not important. On the other hand for the symmetric solutions $G(r, r, \pi)$ are not important. It will be noted also that both the differential equation and the variational one involve simultaneously a function of r_1, r_2, θ and its transposed and that *the dependence on θ is of primary importance in determining the difference between symmetric and antisymmetric solutions.*

The variational equation corresponding to (10) can be written down by inspection and is

$$\delta\int\left\{\left(\frac{\partial f}{\partial r_1}\right)^2+\left(\frac{\partial f}{\partial r_2}\right)^2+(r_1^{-2}+r_2^{-2})\left[\left(\frac{\partial f}{\partial\theta}\right)^2+\frac{f^2}{\sin^2\theta}\right]+8\pi^2 mh^{-2}(V-E)f^2\right\}dV_{r_1,r_2,\theta}=0 \tag{25}$$

with the equation of condition

$$\int f^2 dV_{r_1,r_2,\theta}=1. \tag{25'}$$

This differs from the equation used by Kellner and Hylleraas only by the term $(r_1^{-2}+r_2^{-2})\ f^2/\sin^2\theta$. Obvious changes of variables to r_1, r_2, r_{12} can of course be made and the elliptic coordinates used by Hylleraas can be introduced here with the same boundary conditions.

Only P terms have been considered here. It is clear, however, that the same can be done for any other value of l. Since closed expressions for the general case are complicated, we do not consider them here.

Appendix

(I) Derivation of equation (4)

This can be derived either by the analytical procedure indicated in the text or else by the following geometrical consideration. The first three terms in (2) are squares of infinitesimal rotation operators about the axes x, y, z. The changes in ψ during a rotation are brought about only through its dependence on θ', ϕ', ϕ. We draw two lines ON, OM in the xy plane with azimuths $-\pi/2+\phi$, ϕ. Resolving a rotation about OX along ON and OM with $ON \perp OM$ the first contributes $\sin\phi'\,\partial/\partial\theta'$. The second must be compounded as a sum of rotations along OZ and 0(1) and give rise to

$$\cos\phi'(\cot\theta'(\partial/\partial\phi')-(\partial/\sin\theta'\partial\phi))$$

The rotation operators are thus found to be

$$L_x=\sin\phi'\frac{\partial}{\partial\theta'}+\cos\phi'\left(\cot\theta'\frac{\partial}{\partial\phi'}-\frac{\partial}{\sin\theta'\partial\phi}\right).$$

$$L_y=-\cos\phi'\frac{\partial}{\partial\theta'}+\sin\phi'\left(\cot\theta'\frac{\partial}{\partial\phi'}-\frac{\partial}{\sin\theta'\partial\phi}\right)$$

$$L_z=\frac{\partial}{\partial\phi'}\cdot$$

Equation (4) is then obtained as

$$[L_x{}^2+L_y{}^2+L_z{}^2+l(l+1)]\psi=0.$$

Usual commutation relations between rotation operators are of course also satisfied by L_x, L_y, L_z.

(II) Derivation of (16) and (24).

On account of spherical symmetry it is sufficient to calculate the variational equation for

$$\psi=F_1-F_2\cos\theta=a\cos\theta'+b\sin\theta'\cos\phi$$

where

$$a=F_1-F_2\cos\theta,\quad b=F_2\sin\theta.$$

The equation to be transformed is (23). The volume element is

$$dx_1\cdots dz_2=r_1{}^2r_2{}^2\sin\theta\sin\theta' dr_1dr_2d\theta d\theta' d\phi d\phi'.$$

We have

$$(\mathrm{grad}_1\,\psi)^2=\left(\frac{\partial\psi}{\partial r_1}\right)^2+r_1{}^{-2}\left[\left(\frac{\partial\psi}{\partial\theta_1}\right)^2+(\sin\theta_1)^{-2}\left(\frac{\partial\psi}{\partial\phi_1}\right)^2\right]$$

$$\frac{\partial\psi}{\partial\theta_1}=-F_1\sin\theta_1+\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right)\frac{\partial\theta}{\partial\theta_1}$$

$$\frac{\partial\psi}{\partial\phi_1}=\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right)\frac{\partial\theta}{\partial\phi_1}.$$

Remembering now that

$$\left(\frac{\partial\theta}{\partial\theta_1}\right)^2+\frac{1}{\sin^2\theta_1}\left(\frac{\partial\theta}{\partial\phi_1}\right)^2=1 \tag{a}$$

we have:

$$\left(\frac{\partial\psi}{\partial\theta_1}\right)^2+\frac{1}{\sin^2\theta_1}\left(\frac{\partial\psi}{\partial\phi_1}\right)^2=F_1{}^2\sin^2\theta_1+\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right)^2$$
$$-2F_1\sin\theta_1\frac{\partial\theta}{\partial\theta_1}\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right).$$

Substituting the value for $\partial\theta/\partial\theta_1$ which follows from the first equation (3) and using the second equation (3)

$$\sin\theta_1\frac{\partial\theta}{\partial\theta_1}=-\sin\theta'\cos\phi$$

Writing further

$$a'=\frac{\partial F_1}{\partial \theta}-\frac{\partial F_2}{\partial \theta}\cos\theta, \qquad b'=\frac{\partial F_2}{\partial \theta}\sin\theta$$

we transform the above expression into:

$$F_1{}^2\sin^2\theta'+(a'\cos\theta'+b'\sin\theta'\cos\phi)^2+2F_1(a'\cos\theta'+b'\sin\theta'\cos\phi)\sin\theta'\cos\phi.$$

Hence

$$\int_0^\pi\int_0^{2\pi}\int_0^{2\pi} r_1{}^{-2}\left[\left(\frac{\partial\psi}{\partial\theta_1}\right)^2+(\sin\theta_1)^{-2}\left(\frac{\partial\psi}{\partial\phi_1}\right)^2\right]\sin\theta' d\theta' d\phi' d\phi$$
$$=\frac{(4\pi)^2}{3r_1{}^2}[F_1{}^2+(1/2)(a'^2+b'^2)+b'F_1].$$

Using the symmetrical expression for the term in $r_2{}^{-2}$ and replacing all integrals of $(a\cos\theta'+b\sin\theta'\cos\phi)^2$ by $(4\pi^2/6)\ (a^2+b^2)$ equation (24) follows at once.

To verify (16) directly we evaluate

$$\frac{\partial^2\psi}{\partial\theta_1{}^2}+\cot\theta_1\frac{\partial\psi}{\partial\theta_1}+\frac{\partial^2\psi}{\sin^2\theta_1\partial\phi_1{}^2}\cdot$$

Remembering that

$$\left(\frac{\partial^2}{\partial\theta_1{}^2}+\cot\theta_1\frac{\partial}{\partial\theta_1}+\frac{\partial^2}{\sin^2\theta_1\partial\phi_1{}^2}\right)\theta=\cot\theta$$

and the relation (a), the above expression reduces to

$$\cos\theta_1\left[\frac{\partial^2F_1}{\partial\theta^2}+3\cot\theta\frac{\partial F_1}{\partial\theta}-2F_1\right]-\cos\theta_2\left[\frac{\partial^2F_2}{\partial\theta^2}+\cot\theta\frac{\partial F_2}{\partial\theta}+\frac{2\partial F_1}{\sin\theta\partial\theta}\right]$$

similarly for

$$\frac{\partial^2}{\partial\theta_2{}^2}+\cot\theta_2\frac{\partial}{\partial\theta_2}+\frac{\partial^2}{\sin^2\theta_2\partial\phi_2{}^2}\cdot$$

Substituting into Schroedinger's equation, (16) follows on requiring independent vanishing of coefficients of $\cos\theta_1$, $\cos\theta_2$.