THEORETICAL CHEMISTRY INSTITUTE

THE UNIVERSITY OF WISCONSIN

A PARTIAL WAVE EXPANSION IN SPHEROIDAL COORDINATES

FOR DIATOMIC MOLECULES

by

R. B. Hake

and

W. Byers Brown

WIS-TCI-177 25 July 1966

MADISON, WISCONSIN

A PARTIAL WAVE EXPANSION IN SPHEROIDAL COORDINATES FOR DIATOMIC MOLECULES*

by

R. B. Hake and W. Byers Brown

* This research was supported by the following grant: National Aeronautics and Space Administration NsG-275-62.

Introduction

The method of partial wave expansion has been adopted a number of times in the theoretical investigation of the structure and properties of atoms and one- and two-electron diatomic molecules[1]. The method consists of writing the wave function of the system in the form (for a one-electron system)

$$\Psi = \sum_{\ell, m} \Psi_{\ell m}(r)\, Y_\ell^m(\cos\theta, \phi) \tag{1}$$

where $Y_\ell^m(\cos\theta, \phi)$ are the surface harmonics. This has the advantage that it affords a straightforward method of successive approximation to the total wave function. In applications of this method to diatomic systems the expansion (1) has been made about some point in the molecular framework, such as the centre of charge. One might expect that, for diatomic molecules a more rapidly convergent partial wave expansion could be obtained by employing prolate spheroidal coordinates, which provide a natural coordinate system.

For the diatomic system AB in which the nuclei A and B are separated by a distance R as shown in Figure 1,

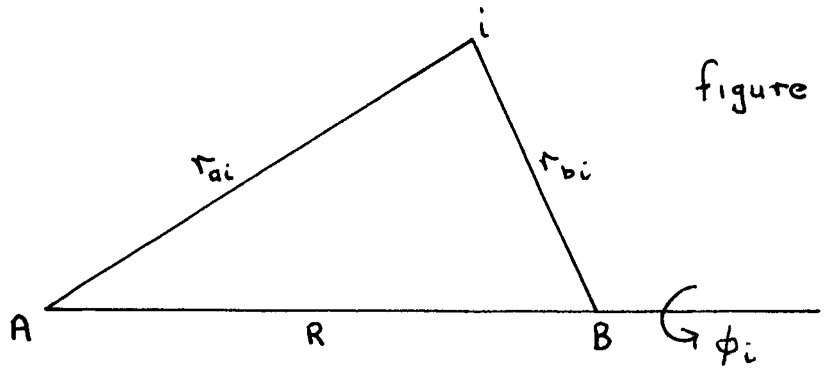

figure 1

we define

$$\xi_i = \frac{r_{ai} + r_{bi}}{R} \quad , \quad \eta_i = \frac{r_{ai} - r_{bi}}{R}$$

and ϕ_i is the angular coordinate of the point i about the internuclear axis.

Application to the N-electron diatomic molecule

A space component of the total wave function for an N-electron diatomic system may be written as

$$\Psi = \sum_{\{\ell,m\}} \Psi_{\{\ell m\}}(\xi_1, \xi_2 \dots \xi_N, R) \times Y_{\ell_1}^{m_1}(\eta_1, \phi_1) \dots Y_{\ell_N}^{m_N}(\eta_N, \phi_N) \tag{2}$$

where the summation is over all values of ${}_1$ - ${}_2$ --- ${}_N$ and permissible values of m_1, m_2 --- m_N , i.e. $|m_i| \leqslant \ell_i$ and also we must have

$$\sum_{j=1}^{N} m_j = M$$

where

$$\mathcal{L}_z \Psi = M \Psi$$

and

$$\mathcal{L}_z = -i \sum_{j=1}^{N} \frac{\partial}{\partial \phi_j}$$

Also

$$\Psi_{\{\ell m\}}(\xi_1, \xi_2 \ldots \xi_N, R) \equiv \Psi_{\ell_1 \ell_2 \ldots \ell_N : m_1 m_2 \ldots m_N}(\xi_1, \xi_2 \ldots \xi_N, R)$$

The expansion (2) is formally exact; however, in all practical applications the series must be truncated. The number of terms retained in the truncated expansion will determine the degree of approximation.

If the nuclear charges in the diatomic system are Z_a and Z_b the Hamiltonian may be written (using prolate spheroidal coordinates)

$$H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{2}{R} \sum_{i=1}^{N} \left(\frac{\sigma \xi_i + \Delta \eta_i}{\xi_i^2 - \eta_i^2} \right) + \sum_{i>j} \frac{1}{r_{ij}} \tag{3}$$

where $\sigma = Z_a + Z_b$: $\Delta = Z_b - Z_a$

and

$$\nabla_i^2 = \frac{4}{R^2(\xi_i^2-\eta_i^2)}\left\{\frac{\partial}{\partial \xi_i}\left[(\xi_i^2-1)\frac{\partial}{\partial \xi_i}\right]+\frac{\partial}{\partial \eta_i}\left[(1-\eta_i^2)\frac{\partial}{\partial \eta_i}\right]\right.$$

$$\left. + \frac{(\xi_i^2-\eta_i^2)}{(\xi_i^2-1)(1-\eta_i^2)}\frac{\partial^2}{\partial \phi_i^2}\right\}$$

and

$$\frac{1}{r_{ij}} = \frac{2}{R}\sum_{L=0}^{\infty}\sum_{M=-L}^{+L}(-1)^M(2L+1)\left[\frac{(L-|M|)!}{(L+|M|)!}\right]^2$$

$$\times P_L^{|M|}[\xi(a)]\,Q_L^{|M|}[\xi(b)]\,P_L^{|M|}(\eta_i)\,P_L^{|M|}(\eta_j)\,e^{iM(\phi_i-\phi_j)}$$

where $\xi(a)$ is the lesser and $\xi(b)$ the greater of ξ_i and ξ_j

We now wish to take the wave equation

$$H\Psi = E\Psi \tag{4}$$

multiply through by the product

$$Y_{\lambda_1}^{\mu_1 *}(\eta_1,\phi_1)\,Y_{\lambda_2}^{\mu_2 *}(\eta_2,\phi_2)\,.\,.\,.\,.\,.\,Y_{\lambda_N}^{\mu_N *}(\eta_N,\phi_N) \tag{5}$$

and integrate over the 'angular' variables η and ϕ . If this is done for every product of the form (5) then a set of equations describing the $\Psi_{\{\ell m\}}(\xi_1, \xi_2 \ldots, \xi_N, R)$ is obtained.

In the following we shall find it convenient to introduce the rotation

$$\Psi\{\ell m\} \equiv \Psi\{\ell_1, \ell_2 \ldots \ell_N : m_1, m_2 \ldots m_N\}$$

$$\Psi[a_i, a_j \ldots a_k : b_i, b_j \ldots b_k]$$

$$\equiv \Psi\{\lambda_1, \lambda_2 \ldots a_i \ldots a_j \ldots a_k \ldots \lambda_N : \mu_1, \mu_2 \ldots b_i \ldots b_j \ldots b_k \ldots \mu_N\}$$

$$\Psi[0] \equiv \Psi\{\lambda_1, \lambda_2 \ldots \lambda_N : \mu_1, \mu_2 \ldots \mu_N\}$$

$$Y_\ell^m(i) \equiv Y_\ell^m(\eta_i, \phi_i)$$

Write the total Hamiltonian as

$$H = h + \sum_{i>j} \frac{1}{r_{ij}}$$

(c.f. equation (3))

$$\text{i)}\quad h\Psi = \sum_{\{lm\}} Y_{l_1}^{m_1}(1)\ldots Y_{l_N}^{m_N}(N)\left\{\sum_{i=1}^{N}\frac{-2}{R^2(\xi_i^2-\eta_i^2)}\right.$$

$$\times\left[(\xi_i^2-1)\frac{\partial^2\Psi\{lm\}}{\partial\xi_i^2} + 2\xi_i\frac{\partial\Psi\{lm\}}{\partial\xi_i} + \left(R\sigma\xi_i - l_i(l_i+1)\right.\right.$$

$$\left.\left.\left. - \frac{m_i^2}{(\xi_i^2-1)} + R\Delta\eta_i\right)\Psi\{lm\}\right]\right\} \qquad (6)$$

Multiply (6) by the product (5) and integrate over the variables η and ϕ for all of the electrons, making use of integrals given by Livingston[2], special cases of which are given in the appendix.

This gives

$$-\frac{2}{R^2}\sum_{i=1}^{N}\left\{\sum_{k_i=0}^{\alpha_i}\left[\left\{(\xi_i^2-1)\frac{\partial^2\Psi[\beta_i:\mu_i]}{\partial\xi_i^2} + 2\xi_i\frac{\partial\Psi[\beta_i:\mu_i]}{\partial\xi_i}\right.\right.\right.$$

$$\left. -\left(\frac{\mu_i^2}{\xi_i^2-1} + \beta_i(\beta_i+1) - R\sigma\xi_i\right)\Psi[\beta_i:\mu_i]\right\}\frac{2(-1)^{\mu_i}}{\xi_i}P_{\beta_i}^{\mu_i}(\xi_i)\,Q_{\lambda_i}^{\mu_i}(\xi_i)$$

$$\left.\times G(\beta_i\lambda_i:\mu_i) + R\Delta 2(-1)^{\mu_i}P_{\gamma_i}^{\mu_i}(\xi_i)\,Q_{\lambda_i}^{\mu_i}(\xi_i)\,\Psi[\gamma_i:\mu_i]\,G(\gamma_i\lambda_i:\mu_i)\right]$$

$$+\sum\Big[\Big\{(\xi_i^2-1)\frac{\partial^2\Psi[\beta_i:\mu_i]}{\partial\xi_i^2} + 2\xi_i\frac{\partial\Psi[\beta_i:\mu_i]}{\partial\xi_i} - \Big(\frac{\mu_i^2}{\xi_i^2-1}$$

$$+\beta_i(\beta_i+1) - R\sigma\xi_i\Big)\Psi[\beta_i:\mu_i]\frac{2(-1)^{\mu_i}}{\xi_i}P_{\lambda_i}^{\mu_i}(\xi_i)\,Q_{\beta_i}^{\mu_i}(\xi_i)\,G(\beta_i\lambda_i:\mu_i)$$

$$+R\Delta 2(-1)^{\mu_i}P_{\lambda_i}^{\mu_i}(\xi_i)\,Q_{\gamma_i}^{\mu_i}(\xi_i)\,\Psi[\gamma_i:\mu_i]\,G(\gamma_i\lambda_i:\mu_i)\Big]\Big\} \qquad (7)$$

where

$$\left.\begin{aligned}\alpha_i &= \lambda_{i/2}\\ \beta_i &= 2\,k_i\\ \gamma_i &= 2\,k_1+1\end{aligned}\right\}\lambda_i \text{ even} \qquad \left.\begin{aligned}\alpha_i &= (\lambda_i-1)/2\\ \beta_i &= 2k_i+1\\ \gamma_i &= 2k_i\end{aligned}\right\}\lambda_i \text{ odd}$$

$$G(a\,b:m) = \left\{\frac{(2a+1)(2b+1)}{4}\,\frac{(a-|m|)!}{(a+|m|)!}\,\frac{(b-|m|)!}{(b+|m|)!}\right\}^{1/2}$$

ii) Consider one of the $1/r_{ij}$ terms multiplied by the product (5).

We have

$$Y_{\lambda_1}^{\mu_1 *}(1) \ldots Y_{\lambda_N}^{\mu_N *}(N) \frac{1}{r_{ij}} \Psi$$

$$= \frac{8\pi}{R} \sum_{\{\ell m\}} \sum_{L=0}^{\infty} \sum_{M=-L}^{+L} (-1)^M \left[\frac{(L-|M|)!}{(L+|M|)!} \right] P_L^M[\xi(a)]\, Q_L^M[\xi(b)]$$

$$Y_L^M(i)\, Y_L^{M*}(i)\, Y_{\ell_1}^{m_1}(1) \ldots Y_{\ell_N}^{m_N}(N)\, Y_{\lambda_1}^{\mu_1}(1) \ldots Y_{\lambda_N}^{\mu_N}(N)\, \Psi\{\ell m\}$$

Integrating over the η , ϕ coordinates of all electrons but i and j gives zero for all terms but $\ell_k = \lambda_k \;:\; m_k = \mu_k$ ($k = 1, 2 \ldots N$: not i, j) Integrating over the coordinates η_i , ϕ_i and η_j , ϕ_j gives

$$\int Y_L^M(i)\, Y_{\ell_i}^{m_i}(i)\, Y_{\lambda_i}^{\mu_i *}(i)\, d\eta_i\, d\phi_i$$

$$= \left[\frac{(2L+1)(2\ell_i+1)}{4\pi\;(2\lambda_i+1)} \right]^{1/2} C(L\ell_i\lambda_i : M m_i \mu_i)\, C(L\ell_i\lambda_i : 000)$$

where $M + m_i - \mu_i = 0$

and the C's are the Clebsch-Gordon coefficients: see, for example, Rose[3].

Also

$$\int Y_L^{M*}(j)\, Y_{\ell_j}^{m_j}(j)\, Y_{\lambda_j}^{\mu_j *}(j)\, d\eta_j\, d\phi_j$$

$$= \left[\frac{(2L+1)(2\lambda_j+1)}{4\pi\ (2\ell_j+1)}\right]^{1/2} C(L\lambda_j\ell_j : M\mu_j m_j)\, C(L\lambda_j\ell_j : 000)$$

where $M + \mu_j - m_j = 0$

Using these results the total $1/r_{ij}$ term is:

$$\frac{2}{R}\sum_{i>j}\ \sum_{\ell_i,\ell_j}\ \sum_{L=0}^{\infty}\ \sum_{M=-L}^{+L} (-1)^M (2L+1)\left[\frac{(L-|M|)!}{(L+|M|)!}\right]$$

$$\times P_L^M[\xi(a)]\, Q_L^M[\xi(b)] \left\{\frac{(2\ell_i+1)(2\lambda_j+1)}{(2\ell_j+1)(2\lambda_i+1)}\right\}^{1/2} C(L\ell_i\lambda_i : M(\mu_i-M)\mu_i)$$

$$\times C(L\ell_i\lambda_i : 000)\, C(L\lambda_j\ell_j : M\mu_j(M+\mu_j)\, C(L\lambda_j\ell_j : 000)$$

$$\times\ \Psi[\ell_i, \ell_j : (\mu_i - M)_i, (M+\mu_j)_j] \qquad (8)$$

iii) Multiplying the R.H.S. of (4) by (5) and integrating over the η's and ϕ's gives simply

$$E\,\Psi[0] \tag{9}$$

Thus the final result is obtained by writing (7) + (8) = (9)

These rather cumbersome equations may be written in a more compact form if we define

$$D_i \equiv (\xi_i^2-1)\frac{\partial^2}{\partial \xi_i^2} + 2\xi_i \frac{\partial}{\partial \xi_i} - \left(\frac{\mu_i^2}{\xi_i^2-1} + \beta_i(\beta_i+1) - R\sigma\,\xi_i\right)$$

$$F(a,b:i) \equiv 2(-1)^{\mu_i} P_a^{\mu_i}(\xi_i)\, Q_b^{\mu_i}(\xi_i)\, G(a\,b:\mu_i)$$

$$K(L,M:i,j) \equiv (-1)^M (2L+1)\left[\frac{(L-|M|)!}{(L+|M|)!}\right] P_L^M[\xi(a)]\, Q_L^M[\xi(b)]$$

$$\times \left\{\frac{(2\ell_i+1)(2\lambda_j+1)}{(2\ell_j+1)(2\lambda_i+1)}\right\}^{1/2} C(L\,\ell_i\,\lambda_i : M(\mu_i-M)\mu_i)\, C(L\,\ell_i\,\lambda_i : 000)$$

$$\times\, C(L\,\lambda_j\,\ell_j : M\mu_j(M+\mu_j))\, C(L\,\lambda_j\,\ell_j : 000)$$

Hence we obtain:

$$-\frac{2}{R^2}\sum_{i=1}^{N}\left\{\sum_{k_i=0}^{\alpha_i}\left[\left\{D_i\,\Psi[\beta_i:\mu_i]\right\}\frac{1}{\xi_i}F(\beta_i,\lambda_i:i) + R_\Delta F(\gamma_i,\lambda_i:i)\,\Psi[\gamma_i:\mu_i]\right]\right.$$

$$\left.+\sum_{k_i=\alpha_i+1}^{\infty}\left[\left\{D_i\,\Psi[\beta_i:\mu_i]\right\}\frac{1}{\xi_i}F(\lambda_i,\beta_i:i) + R_\Delta F(\lambda_i,\gamma_i:i)\,\Psi[\gamma_i:\mu_i]\right]\right\}$$

$$+\frac{2}{R}\sum_{i>j}\sum_{l_i l_j}\sum_{L=0}^{\infty}\sum_{M=-L}^{+L}K(L,M:i,j)\,\Psi[l_i,l_j:(\mu_i-M)_i,(M+\mu_j)_j]$$

$$= E\,\Psi[0] \qquad (10)$$

for every product of the form (5).

The equations (10) are a set of coupled differential equations which are equivalent to the Schrödinger equation of the system, equation (4). Thus the wave function and energy of the diatomic system may be obtained by solving the differential equations (10) for the functions $\Psi_{\{lm\}}(\xi_1 \ldots \xi_N : R)$

Example of the H_2^+ Ion

Here we discuss briefly the application of the foregoing theory to the simple one-electron problem of the H_2^+ molecular ion, the Schrödinger equation of which is separable in prolate spheroidal coordinates, and has been solved accurately by Bates, Ledsham and Stewart[4] and more recently and more extensively by Peek[5].

The wave function can be written in the form (see (1))

$$\Psi = \sum_{l,m} \Psi_{lm}(\xi, R)\, Y_l^m(\eta, \phi) \tag{11}$$

Multiplying the wave function by $Y_\lambda^{\mu *}(\eta, \phi)$ and integrating gives, using the result (10), and restricting our interest to the ground state where $m = 0$

$$\sum_{k=0}^{\alpha} \left[D\,\Psi\{\beta:0\}\right] \frac{1}{\xi}\, 2\, P_\beta(\xi)\, Q_\lambda(\xi)\, G(\beta, \lambda : 0)$$

$$+ \sum \left[D\,\Psi\{\beta:0\}\right] \frac{1}{\xi}\, 2\, P_\lambda(\xi)\, Q_\beta(\xi)\, G(\lambda, \beta : 0)$$

$$= -\frac{R^2 E}{2}\, \Psi\{\lambda, 0\} \tag{12}$$

This set of equations replaces the original Schrödinger equation, so solutions of these equations will determine the wave function and energy of the system. The accuracy of the results obtained is determined by the point where the summation is truncated.

The exact ground state wave function for H_2^+ may be written as

$$\Psi = \Xi(\xi) \sum_{\ell=0}^{\infty} f(\ell, p)\, P_\ell(\eta) \tag{13}$$

where the $f(\ell, p)$ are constants and

$$p^2 = -\frac{R^2 E}{2}$$

Comparing (13) with (11) we see that

$$\Psi\{\ell : 0\} = \left\{\frac{4\pi}{2\ell+1}\right\}^{1/2} f(\ell, p)\, \Xi(\xi) \tag{14}$$

Using (12) it is now possible to derive a condition which must be satisfied by the f's .

The equation for $\Xi(\xi)$ given in reference (3) is

$$(\xi^2 - 1)\frac{d^2\Xi}{d\xi^2} + 2\xi\frac{d\Xi}{d\xi} + \left(C + 2R\xi - p^2\xi^2\right)\Xi = 0$$

where C is a separation constant. This equation is the same as

$$\mathcal{D}\Xi + [\beta(\beta+1) + C - p^2\xi^2]\Xi = 0$$

Hence

$$\mathcal{D}\Xi(\xi) = [p^2\xi^2 - C - \beta(\beta+1)]\Xi(\xi)$$

$$\therefore \mathcal{D}\Psi\{\beta:0\} = [p^2\xi^2 - C - \beta(\beta+1)]\Psi\{\beta:0\}$$

$$= \left\{\frac{4\pi}{2\beta+1}\right\}^{1/2} f(\beta,p)[p^2\xi^2 - C - \beta(\beta+1)]\Xi(\xi)$$

So from (12) we have

$$\sum_{k=0}^{\alpha}\left\{\frac{4\pi}{2\beta+1}\right\}^{1/2} f(\beta,p)[p^2\xi^2 - C - \beta(\beta+1)]\Xi\frac{1}{\xi}2$$

$$\times P_\beta(\xi)Q_\lambda(\xi)G(\beta\lambda:0)$$

$$+\sum_{k=\alpha+1}^{\infty}\left\{\frac{4\pi}{2\beta+1}\right\}^{1/2} f(\beta,p)[p^2\xi^2 - C - \beta(\beta+1)]\Xi\frac{1}{\xi}2$$

$$\times P_\lambda(\xi)Q_\beta(\xi)G(\lambda\beta:0)$$

$$= p^2\left\{\frac{4\pi}{2\lambda+1}\right\}^{1/2} f(\lambda,p)\Xi(\xi)$$

and from this we obtain

$$f(\lambda,\rho) = \frac{2(2\lambda+1)^{1/2}}{\rho^2}\left\{ \sum_{k=0}^{\alpha} E(\xi,\beta)\, P_\beta(\xi)\, Q_\lambda(\xi)\, f(\beta,\rho) \right.$$

$$\left. + \sum_{k=\alpha+1}^{\infty} E(\xi,\beta)\, P_\lambda(\xi)\, Q_\beta(\xi)\, f(\beta,\rho) \right\} \qquad (15)$$

where $E(\xi,\beta) = \{2\beta+1\}^{-1/2}\left[\rho^2\xi^2 - C - \beta(\beta+1)\right]\frac{1}{\xi}G(\beta,\lambda:0)$

Now

$$Q_n(\xi) = P_n(\xi)\,\frac{1}{2}\log\left(\frac{\xi+1}{\xi-1}\right) - W_{n-1}(\xi)$$

See, for example, Jahnke and Emde[6]. Writing $\Lambda = \frac{1}{2}\log\left(\frac{\xi+1}{\xi-1}\right)$ and substituting into (15) we have

$$f(\lambda,\rho) = \frac{2(2\lambda+1)^{1/2}}{\rho^2}\left\{ \sum_{k=0}^{\alpha} E(\xi,\beta)\, P_\beta\left[P_\lambda\Lambda - W_{\lambda-1}\right] f(\beta,\rho) \right.$$

$$\left. + \sum_{k=\alpha+1}^{\infty} E(\xi,\beta)\, P_\lambda\left[P_\beta\Lambda - W_{\beta-1}\right] f(\beta,\rho) \right\}$$

As $\xi \to 1$, $\Lambda \to \infty$, so for this to be true for <u>all</u> values of we require

$$\frac{2(2\lambda+1)^{1/2}}{p^2}\left\{\sum_{k=0}^{\alpha} E(\xi,\beta)\, P_\beta\, P_\lambda\, f(\beta,p) + \sum_{k=\alpha+1}^{\infty} E(\xi,\beta)\, P_\lambda\, P_\beta\, f(\beta,p)\right\}\Bigg|_{\xi=1} = 0$$

$$\therefore \sum_{k=0}^{\infty} E(\xi,\beta)\, P_\beta\, P_\lambda\, f(\beta,p)\Bigg|_{\xi=1} = 0$$

$$E(1,\beta) = \left[p^2 - C - \beta(\beta+1)\right]\left\{\frac{(2\beta+1)(2\lambda+1)}{4\,(2\beta+1)}\right\}^{1/2}$$

$$P_\lambda(1) = P_\beta(1) = 1$$

$$\therefore \sum_{k=0}^{\infty}\left[p^2 - C - \beta(\beta+1)\right] f(\beta,p) = 0$$

The equation (15) may also be used to derive a three-terms recursion relation for the f's.

Using (15) we first form the sum

$$S = \frac{(\lambda+1)(\lambda+2)(2\lambda-1)}{(2\lambda+5)} f_{\lambda+2} + \frac{\lambda(\lambda-1)(2\lambda+3)}{(2\lambda-3)} f_{\lambda-2}$$

$$+ \frac{1}{(2\lambda+1)} \left\{ (\lambda+1)^2(2\lambda-1) + (2\lambda+3)[\lambda^2 - (2\lambda+1)(2\lambda-1)\xi^2] \right\} f_\lambda$$

Then we find that using the recurrence relation for Q_λ

$$(\lambda+2)(\lambda+1)(2\lambda-1)\, Q_{\lambda+2} + (2\lambda+3)\lambda(\lambda-1)\, Q_{\lambda-2}$$

$$+ \left\{ (\lambda+1)^2(2\lambda-1) + (2\lambda+3)[\lambda^2 - (2\lambda+1)(2\lambda-1)\xi^2] \right\} Q_\lambda = 0$$

and the relationship

$$P_\lambda Q_{\lambda-2} - P_{\lambda-2} Q_\lambda = \frac{(2\lambda-1)}{\lambda(\lambda-1)} \xi$$

$$S = -2\left[p^2\xi^2 - c - \lambda(\lambda+1)\right] \left\{ \frac{(2\lambda+3)(2\lambda-1)}{2p^2} \right\} f_\lambda$$

Thus we have

$$\frac{(\lambda+1)(\lambda+2)(2\lambda-1)}{(2\lambda+5)} f_{\lambda+2} + \frac{\lambda(\lambda-1)(2\lambda+3)}{(2\lambda-3)} f_{\lambda-2}$$

$$+\left\{ \frac{(\lambda+1)^2(2\lambda-1)}{(2\lambda+1)} + \frac{(2\lambda+3)\lambda^2}{(2\lambda+1)} - \left[C+\lambda(\lambda+1)\right]\frac{(2\lambda+3)(2\lambda-1)}{p^2}\right\} f_\lambda$$

$$= 0$$

which gives

$$\frac{(\lambda+1)(\lambda+2)}{(2\lambda+5)(2\lambda+3)} f_{\lambda+2} + \frac{\lambda(\lambda-1)}{(2\lambda-3)(2\lambda-1)} f_{\lambda-2}$$

$$+\left\{\frac{2\lambda(\lambda+1)-1}{(2\lambda+3)(2\lambda-1)} - \frac{1}{p^2}\left[C+\lambda(\lambda+1)\right]\right\} f_\lambda = 0$$

It should also be noted here that the essential difference between the partial wave expansion method and the 'usual' separation treatment arises from the fact that in the latter approach the Schrödinger wave is multiplied through by the factor $(\xi^2-\eta^2)$ in order to facilitate separation. If this is not done then we have a term involving $(\xi^2-\eta^2)^{-1}$ which, when expanded, gives an infinite series.

APPENDIX

Some useful integrals for the foregoing theory are

(1) $$\int_{-1}^{1} \frac{P_\ell(\eta)}{(\xi-\eta)}\, d\eta = 2\, Q_\ell(\xi)$$

(2) $$\int_{-1}^{1} \frac{P_\ell(\eta)}{(\xi+\eta)}\, d\eta = -2\, Q_\ell(-\xi) = (-1)^\ell 2\, Q_\ell(\xi)$$

(3) $$\int_{-1}^{1} \frac{P_\ell(\eta)}{(\xi^2-\eta^2)}\, d\eta = \frac{2}{\xi}\, Q_\ell(\xi) \quad : \ell \text{ even}$$

$$= 0 \quad : \ell \text{ odd}$$

(4) $$\int_{-1}^{1} \frac{\eta\, P_\ell(\eta)}{(\xi^2-\eta^2)}\, d\eta = 2\, Q_\ell(\xi) \quad : \ell \text{ even}$$

$$= 0 \quad : \ell \text{ odd}$$

(5) $$\int_{-1}^{1} \frac{\eta\, P_\ell(\eta) P_n(\eta)}{(\xi-\eta)} d\eta = 2\xi P_\ell(\xi) Q_n(\xi) : \ell \leqslant n$$

(6) $$\int_{-1}^{1} \frac{P_n^m(\eta)\, P_\ell^m(\eta)}{(\xi-\eta)} d\eta = (-1)^m 2 P_\ell^m(\xi) Q_n^m(\xi) : \ell \leqslant n$$

(7) $$\int_{-1}^{1} \frac{P_n^m(\eta) P_\ell^m(\eta)}{(\xi+\eta)} d\eta = (-1)^{\ell+n+m} 2 P_\ell^m(\xi) Q_n^m(\xi)$$

$$\ell \leqslant n$$

(8) $$\int_{-1}^{1} \frac{P_n^m(\eta)\, P_\ell^m(\eta)}{(\xi^2-\eta^2)} d\eta = \frac{(-1)^m 2}{\xi} P_\ell^m(\xi)\, Q_n^m(\xi) : \ell \leqslant n$$

for $n+\ell$ even

$= 0 \quad : n+\ell$ odd

(9) $$\int_{-1}^{1} \frac{\eta\, P_n^m(\eta)\, P_\ell^m(\eta)}{(\xi^2-\eta^2)} d\eta = (-1)^m 2 P_\ell^m(\xi) Q_n^m(\xi) : \ell \leqslant n$$

$n+\ell$ odd

$= 0 \quad n+\ell$ even

References

1. P. Luke, R. Meyerott and W. Clendenin, Phys. Rev. 85, 401 (1952); A. Temkin, J. Chem. Phys. 39, 161 (1963); A. Temkin and A. K. Bhatia, J. Chem. Phys. 42, 644 (1965); H. Rabinovich, J. Chem. Phys. 43, 3144 (1965).
2. P. M. Livingston, J. Math. Phys. 7, 325 (1966).
3. M. E. Rose, "Elementary Theory of Angular Momentum" John Wiley (1957).
4. D. R. Bates, K. Ledsham and A. L. Stewart, Phil. Trans. Roy. Soc. A246, 215 (1953).
5. J. M. Peek, Sandia Corporation Report SC-RR-65-77 (1966).
6. E. Jahnke and F. Emde, "Tables of Function", Dover (1945).