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Two Centre Continuum Coulomb Wavefunctions in the Entire Complex Plane*

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We solve the Schrödinger Equation for an electron moving in the Coulomb field of two charged nuclei. We take proper account of the analytic structure of the solutions and thus determine their mathematical form in the entire complex plane. These general solutions are then used to construct the two-centre analogue of the usual one-centre Coulomb wavefunctions.

Key words: Two centre continuum Coulomb wavefunctions

1. Introduction

The calculation of electron ejection processes in intermediate quasimolecular states formed in heavy-ion collisions requires the computation of coupling matrix elements between bound and continuum states. The oscillating nature of the radial continuum wave functions is a disadvantage in computing such matrix elements, which may be more conveniently calculated by performing the required integrals in the complex radial variable plane. It is therefore convenient to examine the analytic properties of the continuum solutions to the Schrödinger equation, separated in prolate elliptical coordinates.

We shall write the solutions in the form

$$X_{ml}(\xi) = \frac{1}{\xi}\left[\frac{\xi^2 - 1}{\xi^2}\right]^{1/2m} \sum_{n=-\infty}^{\infty} d_{\nu+n}^{ml} F_{\nu+n}(\lambda, c\xi) \tag{1}$$

where ξ is the radial coordinate in a prolate elliptical coordinate system, m is the azimuthal angular momentum, l the asymptotic total angular momentum, $c^2 = \frac{1}{2}ER^2$ where E and R are the energy of the state and internuclear distance, and $\lambda = (Z_1 + Z_2)R/2c$ is the Sommerfeld parameter (Z_1 and Z_2 are the charges on the 2 nuclei). $F_{\nu+n}(\lambda, c\xi)$ is a Coulomb wave function with an angular momentum parameter $\nu + n$ (defined in detail below), and the $d_{\nu+n}^{ml}$ satisfy a recursion relation (RR) discussed further in the text. In Ref. [1] we chose such a form for the solutions but took $\nu = m$. Although this is asymptotically true for $c\xi \gg 1$, $l \gg cR$ the calculation of transition matrix elements requires the use of non-integral values of ν. As we shall show below ν is a parameter which expresses the many

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valued nature of the continuum solutions, and may in general take non-integral values. We begin by considering the general problem and then construct solutions which satisfy the physical boundary conditions. The important mathematical details are given in an appendix.

2. The General Solution of the Schrödinger Equation

2.1. Separation

As in Ref. [1] we work in a system of prolate elliptical coordinates (ξ, η, ϕ) defined by $\xi = (r_1 + r_2)/R$, $\eta = (r_1 - r_2)/R$ with ϕ the angle between the (x, y) plane and the (r_1, r_2) plane. We use $(r, \theta, \tilde{\phi})$ to represent the ordinary spherical polar coordinates. R is the internuclear distance (see Fig. 1). We have

$$\begin{array}{lll} 0 \leqslant \phi \leqslant 2\pi & \phi \equiv \tilde{\phi} & \\ 1 \leqslant \xi < \infty & \xi \to \dfrac{2r}{R} & \text{as } R \to 0 \text{ or } \xi \to \infty \\ -1 \leqslant \eta \leqslant 1 & \eta \to \cos\theta & \text{as } R \to 0 \text{ or } \xi \to \infty \end{array}$$

The potential felt by the electron at $\mathbf{r}$ is

$$V(r, R) = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}$$

where we work in atomic units. Defining

$$\begin{aligned} c^2 &= \tfrac{1}{2}ER^2 \\ p &= (Z_2 - Z_1)R \\ q &= (Z_1 + Z_2)R \\ \lambda &= -q/2c \\ k &= \sqrt{2E} = 2\,c/R \end{aligned}$$

the Schrödinger Equation $[-\frac{1}{2}\nabla^2 + V(r, R)]\,\Psi(r) = E\Psi(\mathbf{r})$ separates [2] to give with $\Psi(\mathbf{r}) = X(\xi)S(\eta)\Phi(\phi)$:

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \qquad (2)$$

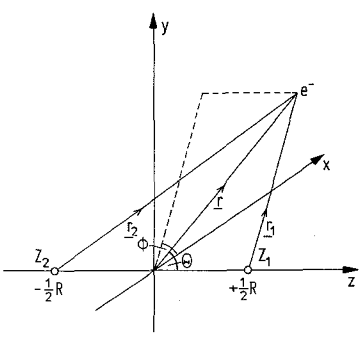


Fig. 1. The coordinate system used

$$\frac{d}{d\eta}(1-\eta^2)\frac{dS}{d\eta}-\frac{m^2 S}{1-\eta^2}+[p\eta+A-c^2\eta^2]S=0 \tag{3}$$

$$\frac{d}{d\xi}(\xi^2-1)\frac{dX}{d\xi}-\frac{m^2 X}{\xi^2-1}+[c^2\xi^2+q\xi-A]X=0 \tag{4}$$

A and m are the separation constants. Eq. (2) may be solved immediately to give $\Phi = 1/\sqrt{2\pi}\, e^{im\phi}$ with the requirement that m is an integer. Since only m^2 appears in Eqs. (3) and (4) we may take m to be a positive integer, or zero. Eqs. (3) and (4) are identical in structure, differing only in the value of p and q. Let us therefore only consider the general solution to Eq. (4) throughout the entire complex plane: this also provides the general solution to Eq. (3) and the solutions which satisfy the physical boundary conditions may then be constructed.

2.2. *The General Solution*

Eq. (4) has three singularities one each at ± 1 with indices $\pm\frac{1}{2}m$, and an essential singularity at ∞. In general these will be branch points of the solution which is many valued. Let us therefore pick $y_1(\xi)$ as a basic solution to Eq. (4) with the property [3]

$$y_1(e^{2i\pi}\xi)=e^{2\pi i\nu}y_1(\xi) \tag{5a}$$

where we have cut the complex plane from +1 to $-\infty$. It is shown in the appendix that a second independent solution $y_2(\xi)$ then exists with the property

$$y_2(e^{2\pi i}\xi)=e^{-2\pi(1+\nu)}y_2(\xi) \tag{5b}$$

ν is called the characteristic exponent, and as will be shown is a function of the parameters of the equation. Let us now construct series expansions for y_1 and y_2. Since these are many valued functions it will be necessary to use a set of many valued functions to represent them. Suitable expansions are [3] for y_1.

$$Qs^m_{-1-\nu}(\xi)=\sum_{n=-\infty}^{\infty} a^m_{-1-\nu+n}Q^m_{-1-\nu+n}(\xi) \tag{6a}$$

$$Fs^m_\nu(\xi)=\frac{1}{\xi}\left[\frac{\xi^2-1}{\xi^2}\right]^{1/2m}\sum_{n=-\infty}^{\infty} d^m_{\nu+n}F_{\nu+n}(\lambda,c\xi) \tag{6b}$$

for y_2:

$$Qs^m_\nu(\xi)=\sum_{n=-\infty}^{\infty} a^m_{\nu+n}Q^m_{\nu+n}(\xi) \tag{6c}$$

$$Fs^m_{-1-\nu}=\frac{1}{\xi}\left[\frac{\xi^2-1}{\xi^2}\right]^{1/2m}\sum_{n=-\infty}^{\infty} d^m_{-1-\nu+n}F_{-1-\nu+n}(\lambda,c\xi) \tag{6d}$$

The following definitions have been used [4]:

$Q_{\nu+n}$ is a Legendre function of the second kind

$F_{\nu+n}$ is a generalized Coulomb wavefunction

$$F_\nu(\lambda,\rho)=\frac{2^\nu[\Gamma(1+\nu-i\lambda)\Gamma(1+\nu+i\lambda)]^{1/2}}{\Gamma(2\nu+2)}\rho^{\nu+1}e^{-i\rho}\,{}_1F_1(1+\nu-i\lambda,2\nu+2,2i\rho) \tag{7}$$

with ${}_1F_1(1+\nu-i\lambda, 2\nu+2, 2i\rho)$ a confluent hypergeometric function of the first kind.

Substituting these expansions in Eq. (4) gives RR's between the coefficients $a^m_{\nu+n}(d^m_{\nu+n})$ which must be satisfied for $Qs^m_\nu(Fs^m_\nu)$ to be solutions. They are

$$w_{n+2}a^m_{\nu+n+2} + v_{n+1}a^m_{\nu+n+1} + u_n a^m_{\nu+n} + t_{n-1}a^m_{\nu+n-1} + s_{n-2}a^m_{\nu+n-2} = 0 \tag{8a}$$

$$w_{n+2} = \frac{(\nu+n+m+1)(\nu+n+m+2)}{(2\nu+2n+3)(2\nu+2n+5)}c^2 \tag{8b}$$

$$v_{n+1} = \frac{(\nu+m+n+1)}{(2\nu+2n+3)}q \tag{8c}$$

$$u_n = (\nu+n)(\nu+n+1) - A + \frac{2(\nu+n)(\nu+n+1)-2m^2-1}{(2\nu+2n-1)(2\nu+2n+3)}c^2 \tag{8d}$$

$$t_{n-1} = \frac{(\nu+n-m)}{(2\nu+2n-1)}q \tag{8e}$$

$$s_{n-2} = \frac{(\nu+n-m)(\nu+n-m-1)}{(2\nu+2n-1)(2\nu+2n-3)}c^2 \tag{8f}$$

$$\tilde{w}_{n+2}d^m_{\nu+n+2} + \tilde{v}_{n+1}d^m_{\nu+n+1} + \tilde{u}_n d^m_{\nu+n} + \tilde{t}_{n-1}d^m_{\nu+n-1} + \tilde{s}_{n-2}d^m_{\nu+n-2} = 0 \tag{9a}$$

$$\tilde{w}_{n+2} = -\frac{[(\nu+n+2)^2+\lambda^2]^{1/2}[(\nu+n+1)^2+\lambda^2]^{1/2}(\nu+n-m+1)(\nu+n-m+2)}{(\nu+n+1)(\nu+n+2)(2\nu+2n+3)(2\nu+2n+5)} \tag{9b}$$

$$\tilde{v}_{n+1} = -\frac{2\lambda m[(\nu+n+1)^2+\lambda^2]^{1/2}(\nu+n-m+1)}{(\nu+n)(\nu+n+1)(\nu+n+2)(2\nu+2n+3)}c^2 \tag{9c}$$

$$\tilde{u}_n = (\nu+n)(\nu+n+1) - A + c^2\left\{\frac{2(\nu+n)(\nu+n+1)-2m^2-1}{(2\nu+2n-1)(2\nu+2n+3)} + \frac{2\lambda^2[(\nu+n)(\nu+n+1)-3m^2]}{(\nu+n)(\nu+n+1)(2\nu+2n-1)(2\nu+2n+3)}\right\} \tag{9d}$$

$$\tilde{t}_{n-1} = \frac{2\lambda m[(\nu+n)^2+\lambda^2]^{1/2}(\nu+n+m)}{(\nu+n-1)(\nu+n)(\nu+n+1)(2\nu+2n-1)}c^2 \tag{9e}$$

$$\tilde{s}_{n-2} = -\frac{[(\nu+n-1)^2+\lambda^2]^{1/2}[(\nu+n)^2+\lambda^2]^{1/2}(\nu+n+m-1)(\nu+n+m)}{(\nu+n-1)(\nu+n)(2\nu+2n-3)(2\nu+2n-1)} \tag{9f}$$

Letting $\nu \to m$ recovers the RR given in Ref. [1] Eq. (16).

An expansion which is more useful for a discussion of the value of the characteristic exponent ν may be obtained by moving the singularities of Eq. (4) to the standard positions $0, 1, \infty$ by the substitution

$$t = \tfrac{1}{2}(\xi+1) \tag{10}$$

A solution is then found to be

$$\tilde{F}s^m_\nu(\xi) = \left[\frac{\xi+1}{\xi-1}\right]^{1/2m} \sum_{n=-\infty}^{\infty} \tilde{d}^m_{\nu+n}\tilde{F}_{\nu+n}[\lambda, c(\xi+1)] \tag{11}$$

with $\tilde{F}_\nu(\lambda, \rho) = 1/\rho F_\nu(\lambda, \rho)$ and where the $\tilde{d}^m_{\nu+n}$ satisfy

$$V_{n+1}\tilde{d}^m_{\nu+n+1} + U_n\tilde{d}^m_{\nu+n} + T_{n-1}\tilde{d}^m_{\nu+n-1} = 0 \tag{12}$$

with

$$V_{n+1} = \frac{-2c[(\nu+n+1)^2+\lambda^2]^{1/2}(\nu+n+m+1)}{(2\nu+2n+3)} \tag{12a}$$

$$U_n = (\nu+n)(\nu+n+1) - A + c^2 \tag{12b}$$

$$T_{n-1} = \frac{-2c[(\nu+n)^2+\lambda^2]^{1/2}(\nu+n-m)}{(2\nu+2n-1)} \tag{12c}$$

2.3. The Solution of the Recursion Relation and the Value of the Characteristic Exponent

From Eq. (12) we have

$$R_n(\nu) \equiv \frac{\tilde{d}^m_{\nu+n}}{\tilde{d}^m_{\nu+n-1}} = \frac{-T_{n-1}}{U_n + V_{n+1}(\tilde{d}^m_{\nu+n+1}/\tilde{d}^m_{\nu+n})} \tag{13a}$$

and

$$L_n(\nu) \equiv \frac{\tilde{d}^m_{\nu+n}}{\tilde{d}^m_{\nu+n+1}} = \frac{-V_{n+1}}{U_n + T_{n-1}(\tilde{d}^m_{\nu+n-1}/\tilde{d}^m_{\nu+n})} \tag{13b}$$

It is shown in the appendix that $R_n(\nu) \sim c/n$ or n/c for large n, and similarly for $L_n(\nu)$. For $n \gg 1$ we require the convergent solution $R_n(\nu) \sim c/n$ and for $n \ll -1$ we require the solution $L_n(\nu) \sim c/n$. Let us therefore pick some large positive value $N \gg 1$ and ignore the term $V_{N+1}[(\tilde{d}^m_{\nu+N+1})/(\tilde{d}_{\nu+N})]$ (which is of order c^2) in comparison with U_N (which is of order N^2). This enables us to calculate $R_N(\nu)$ and since

$$R_{n-1}(\nu) = \frac{-T_{n-2}}{U_{n-1} + V_nR_n(\nu)}$$

we may calculate all $R_n(\nu)$ for $n < N$. Similarly we may calculate all $L_n(\nu)$ for all $n > N^*$ where N^* is some large negative number. We then have

$$\tilde{d}^m_{\nu+n} = \tilde{d}^m_\nu \prod_{r=1}^{n} R_r(\nu) \qquad n > 0 \tag{14a}$$

$$\tilde{d}^m_{\nu+n} = \tilde{d}^m_\nu \prod_{r=-1}^{n} L_n(\nu) \qquad n < 0 \tag{14b}$$

which both provide convergent solutions. The condition that the two series defined in this way give a solution to the differential Eq. (4) is obviously

$$R_1(\nu)L_0(\nu) = \frac{\tilde{d}^m_{\nu+1}}{\tilde{d}^m_\nu} \cdot \frac{\tilde{d}^m_\nu}{\tilde{d}^m_{\nu+1}} = 1$$

If ν is an integer $= l$ say then the series defined from Eq. (12) terminates, and provides a solution to Eq. (4) under the condition

$$L_{-m-l} + \frac{U_{-m-l}}{V_{-m-l+1}} = 0$$

Hence defining

$$\mathscr{F}(\nu, A) = R_1(\nu) L_0(\nu) - 1 \qquad \nu \neq \text{integer} \tag{15a}$$

$$\mathscr{F}(l, A) = L_{-m-l} + \frac{U_{-m-l}}{V_{-m-l+1}} \qquad \nu = l = \text{integer} \tag{15b}$$

the condition that the series defined by the RR 12 is a solution to Eq. (4) is

$$\mathscr{F}(\nu, A_\nu) = 0 \tag{16}$$

Clearly $\mathscr{F}$ also depends upon the parameter c, λ, m. Hence specifying these parameters implicitly determines a relationship between the characteristic exponent ν and the separation constant A_ν. In Ref. [1] it was assumed that the characteristic exponent could be chosen to be m, and the separation constant simultaneously chosen to be A_l. It is shown in the appendix that this is only possible if $|p| = |q|$; i.e. Z_1 or $Z_2 = 0$. This corresponds to the one-centre problem in prolate elliptical coordinates [5].

Since Legendre functions of the first kind $P^m_{\nu+m}$ satisfy same RR as those of the second kind [4] another solution may be obtained from Eqs. (6a) and (6c), i.e.

$$Ps^m_\nu(\xi) = \sum_{n=-\infty}^{\infty} a^m_{\nu+n} P^m_{\nu+n}(\xi) \tag{17}$$

In order to fix the normalization for these model solutions we shall require $a^m_\nu = d^m_\nu = \tilde{d}^m_\nu = a^m_{-1-\nu} = d^m_{-1-\nu} = \tilde{d}^m_{-1-\nu} = 1$.

3. The Physical Solutions

3.1. Convergence

We have described a process for deriving solutions to the second order differential Eq. (4). It is shown in the appendix that these solutions converge in the complex plane cut from +1 to $-\infty$ under the following circumstances.

Qs^m_ν; $Qs^m_{-1-\nu}$:	everywhere except at ± 1 where the solutions possess singularities
Fs^m_ν; $Fs^m_{-1-\nu}$:	everywhere in the region $\|\xi\| > 1$
$\tilde{F}s^m_\nu$; $\tilde{F}s^m_{-1-\nu}$:	everywhere in the region $\|\xi + 1\| > 2$
Ps^m_ν:	everywhere except -1 where there is a singularity

There also exist the solutions

$$\mathbb{P}s^m_\nu = \sum_{n=-\infty}^{\infty} a^m_{\nu+n} \mathbb{P}^m_{\nu+n}(\xi) \tag{18}$$

which converge on the interval $-1 < \xi \leqslant 1$. Here $\mathbb{P}^m_{\nu+n}$ is the Legendre function defined on the cut [4].

3.2. The Angular Solutions

As we have indicated Eqs. (3) and (4) are identical differing only in the values of the parameters p and q. Thus provided $-p$ is substituted for q in Eqs. (8b) and (8d) and the Sommerfeld parameter $\lambda = -q/2c$ is replaced by $\lambda' = p/2c$ wherever it occurs, the solutions developed in the previous sections are also applicable to Eq. (3).

Now the angular solutions are required in the region $-1 \leqslant \eta \leqslant 1$ and therefore Eq. (18) is the appropriate choice.

$$S(\eta) \sim \mathbb{P}s_\nu^m(\eta) = \Sigma \alpha_{\nu+n}^m \mathbb{P}_{\nu+n}^m(\eta)$$

where $\alpha_{\nu+n}^m$ satisfies the RR 8 with $-p$ substituted for q in (8b) and (8d), and $\alpha_\nu^m = 1$. We have already remarked that this solution converges everywhere in $-1 < \eta \leqslant 1$, but in general it has a singularity at $\eta = -1$. However if ν is chosen to be an integer $= l$ say then $\mathbb{P}s_\nu^m(\eta)$ has no singularity at $\eta = -1$ and provides a regular solution in the region $-1 \leqslant \eta \leqslant 1$. Eq. (16) then determines the allowed values of the separation constant A_l. Thus the value of the separation constant is specified by the requirement that the angular solution should have no singularities, in exactly the same way as the separation constant in the spherically symmetric case is required to be of the form $l(l+1)$ where l is integer (the orbital angular momentum quantum number) so that the angular solution $\mathbb{P}_l^m(\cos\theta)$ has no singularity at $\theta = \pi$.

Once A and ν have been specified the expansion coefficients α_{l+n} may be calculated by the methods outlined in the appendix and the angular solution may be written

$$S_{ml}(\eta) = N_A \mathbb{P}s_l^m(\eta) = \sum_{n=m-l}^{\infty} \alpha_{l+n}^m \mathbb{P}_{l+n}^m(\eta) \tag{19}$$

N_A is chosen so that $\int_{-1}^{1} [S_{ml}(\eta)]^2 d\eta = 2/(2l+1)\,(l+m)!/(l-m)!$, i.e.

$$N_A = \left\{ \sum_{n=m-l}^{\infty} (\alpha_{l+n}^m)^2 \frac{2}{(2n+2l+1)} \frac{(l+n+m)!}{(l+n-m)!} \right\}^{-1/2} \left\{ \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} \right\}^{1/2} \tag{20}$$

3.3. The Radial Solution

The radial solution $X_{ml}(\xi)$ is required for the region $1 \leqslant \xi < \infty$. All the model solutions converge in this region but the solutions Fs_ν^m, Qs_ν^m, $Fs_{-1-\nu}^m$, $Qs_{-1-\nu}^m$ all have singularities at $\xi = 1$ unless ν is an integer. Since A_l has already been specified the value of ν is determined through Eq. (16) and assuming $|p| \neq |q|$ (i.e. assuming there are two charged centres) ν cannot be integral. Therefore the only acceptable solution is

$$X_{ml} = N_R \, Ps_\nu^m(\xi) = N_R \sum_{n=-\infty}^{\infty} a_{\nu+n}^m P_{\nu+n}^m(\xi) \tag{21}$$

In the spherically symmetric case the analogous solution is $1/rF_l(\lambda, kr)$ where $F_l(\lambda, kr)$ is a Coulomb wavefunction, and k has previously been defined as the asymptotic electron momentum [6]. This solution has the asymptotic form

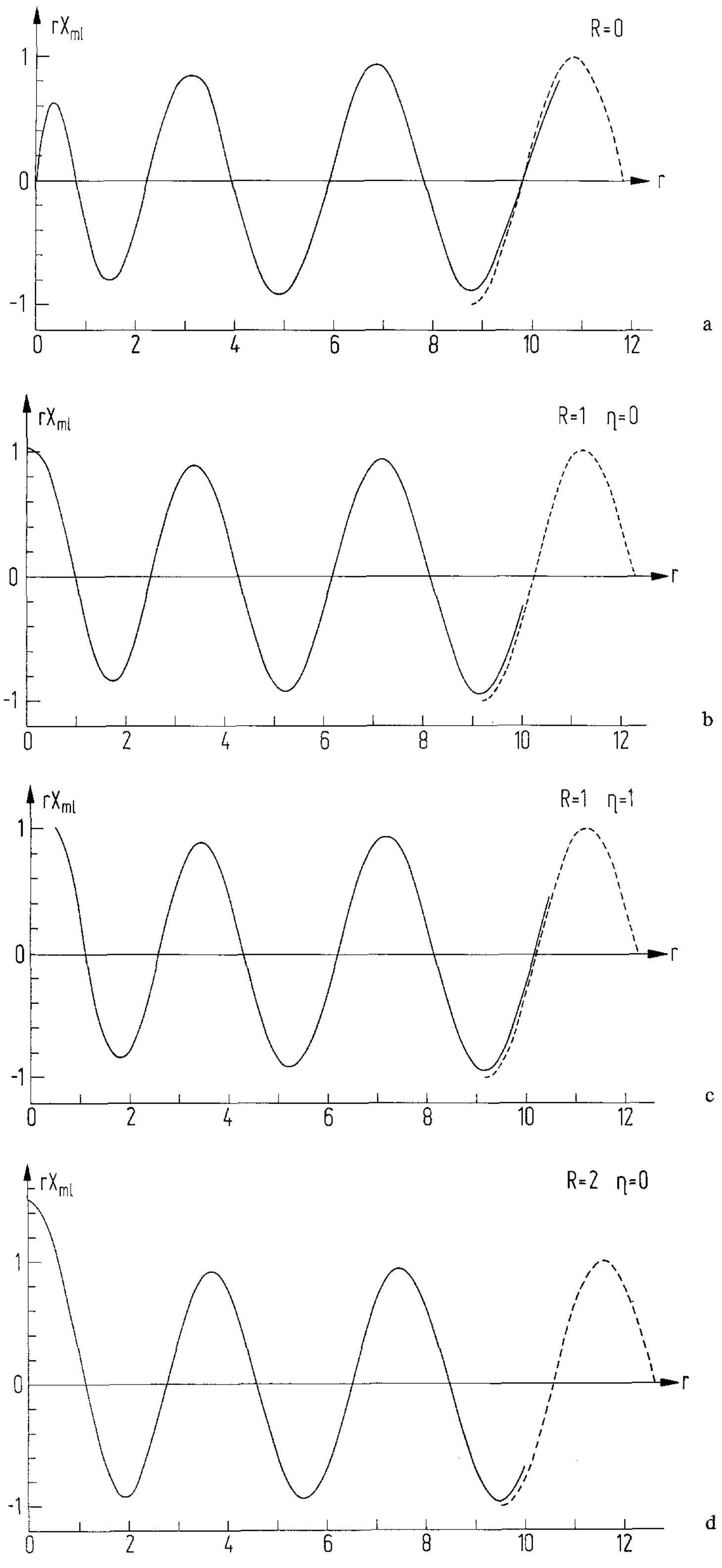
$$F_l(\lambda, kr) \xrightarrow[r\to\infty]{} \sin(kr - \lambda \ln(2kr) + \Theta_l^{(1)})$$

where $\Theta_l^{(1)}$ is the Coulomb phase shift. We shall show that N_R may be chosen so that as $\xi \to \infty$

$$X_{ml}(\xi) \xrightarrow[\xi\to\infty]{} \frac{1}{r} \sin(kr - \lambda \ln(2kr) + \Theta_{ml}^{(2)}) \tag{22}$$

$\Theta_{ml}^{(2)}$ then represents the two-centre Coulomb phase shift.

Eq. (4) is a second order differential equation and thus possesses only two independent solutions. We have, however, given a total of seven, and hence any three of them must be linearly related. We take advantage of this to display the asymptotic form of $Ps_\nu^m(\xi)$.



rX_ml
R=0
1
0
-1
r
0
2
4
6
8
10
12
a
rX_ml
R=1 η=0
b
rX_ml
R=1 η=1
c
rX_ml
R=2 η=0
d

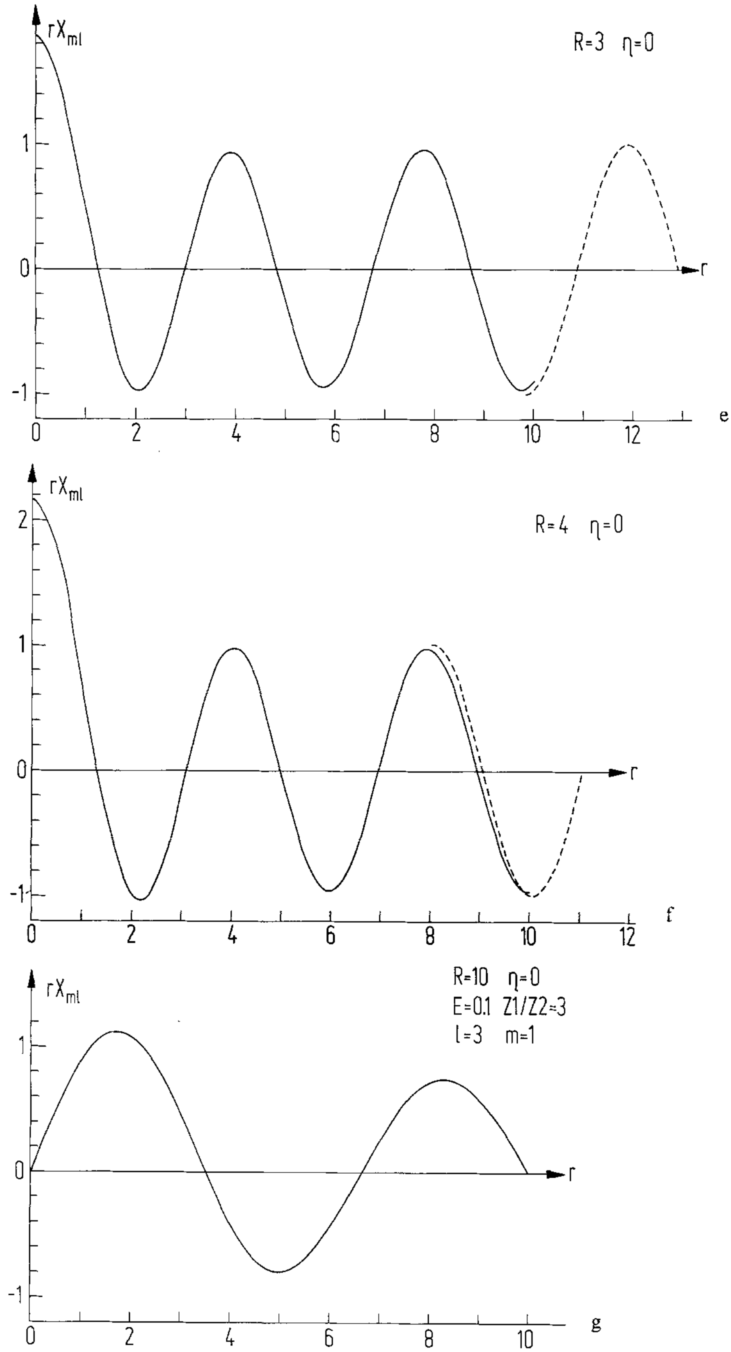


Fig. 2. Examples of two-centre wave functions $rX_{ml}[\Gamma(\xi, \eta)]$

a $R = 0$ a.u. $\eta = \cos\theta$
b $R = 1$ a.u. $\eta = 0$
c $R = 1$ a.u. $\eta = 1$
d $R = 2$ a.u. $\eta = 0$
e $R = 3$ a.u. $\eta = 0$
f $R = 4$ a.u. $\eta = 0$

(a–f:) $E = 1$ a.u. $l = 0$, $m = 0$ $z_1/z_2 = 1$. The dashed line is the asymptotic form for the wavefunction i.e. $\sin(kr - \lambda\ln(2kr) + \Theta_{ml}^{(2)})$

g $R = 10$ a.u. $\eta = 0$ $E = 0.1$ a.u. $l = 3$, $m = 1$ $z_1/z_2 = 3$

It is easy to show that [7]

$$Ps_\nu^m(\xi) = \frac{1}{\pi}\tan(\pi\nu)\{Qs_\nu^m(\xi) - Qs_{-1-\nu}^m(\xi)\} \tag{23}$$

Furthermore it is shown in the appendix that

$$Qs_{-1-\nu}^m(\xi) = H_\nu^{(a)}(j) Fs_\nu^m(\lambda, c\xi) \tag{24a}$$

with

$$H_\nu^{(a)}(j) = -\frac{\pi^{1/2}\cot(\pi\nu)}{c^{(1+\nu+j)}\Gamma(l+n-m)!} \times \\ \times \frac{\sum\limits_{n=0}^{\infty} a_{\nu+j+2n}^m \dfrac{\Gamma(\frac{1}{2}+\nu+j+n)}{n!}(-1)^n}{\sum\limits_{k=0}^{\infty} d_{\nu+j-k}^m \left[\dfrac{\Gamma(1+\nu+j-k+i\lambda)}{\Gamma(1+\nu+j-k-i\lambda)}\right]^{1/2} (i)^k \sum\limits_{s=0}^{k} \dfrac{(-\frac{1}{2})^{k-s}\Gamma(1+\nu+j+s-k-i\lambda)}{s!(k-s)!\Gamma(2\nu+2j+2-2k+s)}} \tag{24b}$$

Now from the definition of Fs_ν^m and the asymptotic form of $F_{\nu+n}(\lambda, c\xi)$ we have for the asymptotic form of Fs_ν^m

$$Fs_\nu^m(\lambda, c\xi) \xrightarrow[\xi\to\infty]{} \frac{1}{\xi}\{A_\nu e^{ic\xi - i\lambda\ln(2c\xi)} + B_\nu e^{-ic\xi + i\lambda\ln(2c\xi)}\} \tag{25a}$$

with

$$A_\nu = \tfrac{1}{2}e^{(1/2)\pi\lambda}e^{-i\pi(\nu+1)/2} \sum_{n=-\infty}^{\infty} d_{\nu+n}^m \left[\frac{\Gamma(1+\nu+n+i\lambda)}{\Gamma(1+\nu+n-i\lambda)}\right]^{1/2} e^{-i\pi n/2} \tag{25b}$$

$$B_\nu = \tfrac{1}{2}e^{(1/2)\pi\lambda}e^{i\pi(\nu+1)/2} \sum_{n=-\infty}^{\infty} d_{\nu+n}^m \left[\frac{\Gamma(1+\nu+n-i\lambda)}{\Gamma(1+\nu+n+i\lambda)}\right]^{1/2} e^{i\pi n/2} \tag{25c}$$

and therefore defining

$$\mu_\nu^\pm = H_\nu^{(a)}(j)(A_\nu \pm B_\nu)$$

$$\gamma_\pm = \mu_\nu^\pm + \mu_{-1-\nu}^\pm$$

we have

$$\xi Ps_\nu^m(\xi) \xrightarrow[\xi\to\infty]{} \frac{1}{\pi}\tan(\pi\nu)\{\gamma_+\cos(c\xi - \lambda\ln(2c\xi)) + i\gamma_-\sin(c\xi - \lambda\ln(2c\xi))\}$$

or

$$Ps_\nu^m(\xi) \xrightarrow[\xi\to\infty]{} \tfrac{1}{2}R\tilde{N}^{-1}\frac{\tan(\pi\nu)}{\pi}\sin(kr - \lambda\ln(2kr) + \Theta_{ml}^{(2)})$$

where $\tilde{N} = (\gamma_+^2 + \gamma_-^2)^{1/2}$; $\tan\Theta_{ml}^{(2)} = -i\gamma_+/\gamma_-$ and hence taking $N_R = \pi/[\tan(\pi\nu)]\cdot(2/R)\tilde{N}$ gives

$$X_{ml}(\xi) = N_R Ps_\nu^m(\xi) \xrightarrow[\xi\to\infty]{} \frac{1}{r}\sin(kr - \lambda\ln(2kr) + \Theta_{ml}^{(2)}) \tag{26}$$

as the radial solution.

Thus asymptotically the one-centre and two-centre solutions differ only by a phase shift, as indeed they must. Several examples are given in Fig. 2.

4. Conclusions

The differential Eq. (4) has an extra degree of complexity with respect to that arising in the one-centre case, since it possesses one more singularity. This further complexity manifests itself in two ways. First, the solutions to the equation are most easily expressed as a series of higher transcendental functions which possess three simple singularities ($P^m_{\nu+n}$, $Q^m_{\nu+n}$) or one simple and one essential singularity ($F_{\nu+n}$). Secondly the characteristic exponent ν must be defined and is, in general, non-integral. The physical solutions, however, may be constructed in a rather direct way from the general solutions (Eqs. (6), (11)) and possess the expected properties.

The phase shift calculated from Eq. (26) have been compared to those given in Ref. [8] for selected values of the parameters, and a systematic difference is found, i.e.

$$\text{phase shift (Ref. [8])} - \text{phase shift (this work)} = \tfrac{1}{2}\,\mathrm{kR}$$

We have therefore checked selected results by writing

$$Ps^m_\nu(\xi) = \alpha Fs^m_\nu(\lambda, c\xi) + \beta Fs^m_{-1-\nu}(\lambda, c\xi)$$

and evaluating the functions Ps^m_ν, Fs^m_ν, $Fs^m_{-1-\nu}$ at two points so that α and β may be calculated. These values are then checked by evaluating the functions at a 3rd point. The asymptotic form of Fs^m_ν, $Fs^m_{-1-\nu}$ rather than $\tilde{F}s^m_\nu$, $\tilde{F}s^m_{-1-\nu}$ (see appendix) are then used to evaluate the phase shift, which is found to agree with the results of Eq. (A14). We may also note that in cases where the characteristic exponent ν is complex the reality of the calculated phase shift $\Theta^{(2)}_{ml}$ also provides a check on the method.

Finally we may examine the shortcomings of Ref. [1]. From Eq. (A25) and the asymptotic form for $A_\nu(\nu \to \infty)$ it can be shown that for large l values ($l \gg kR$) the characteristic ν is very close to an integer. In this case we might expect that the principal component of the

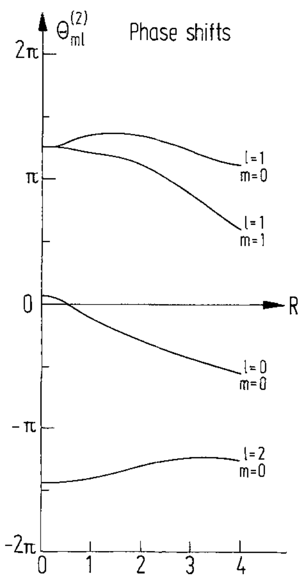


Fig. 3. The phase shifts $\Theta^{(2)}_{ml}$

Table 1. Values of the characteristic exponent ν and the expansion coefficients α and β defined by $\tilde{P}s_\nu^m = \tilde{\alpha}\tilde{F}s_\nu^m + \tilde{\beta}\tilde{F}s_{-1-\nu}^m$. In all cases we take $m = 0, E = 1$ and $Z_1 = Z_2$. R, the internuclear distance, is measured in atomic units. It can be seen that $|\tilde{\alpha}/\tilde{\beta}| \to 0$ (or ∞) for $l/(kR) \to \infty$

$l = 0$

R	ν	$\tilde{\alpha}$	$\tilde{\beta}$
1	1/2 + 0.42869i	0.5518 + 1.7857i	1.19148 − 1.4251i
2	1/2 + 0.87797i	0.18249 + 0.12647i	0.20472 − 0.08595i
3	1/2 + 1.14247i	0.065683 + 0.011738i	0.067882 − 0.00457i
4	1/2 + 1.37781i	0.026969 + 0.007814i	0.02770 + 0.00462i

$l = 1$

R	ν	$\tilde{\alpha}$	$\tilde{\beta}$
0.9	0.90971	14.027 − 1.3768i	−1.6287 + 0.1599i
2	0.133134	−1.8933 + 1.5069i	3.7047 − 2.9485i
3	1/2 + 0.31305i	−1.3067 − 1.2405i	0.67453 + 1.6707i
4	1/2 + 0.81532i	−0.19955 − 0.00656i	0.01571 + 0.19903i

$l = 2$

R	ν	$\tilde{\alpha}$	$\tilde{\beta}$
1	0.978177	−50.063 + 75.794i	0.1166 − 0.1766i
2	0.113004	−0.0135 − 0.9108i	0.1770 + 11.942i
3	0.313251	−0.001422 − 3.22361i	0.002849 + 6.4567i
4	0.390713	−0.43137 − 5.83615i	0.53183 + 7.1953i

two-centre wave function is just Fs_ν^m (or $Fs_{-1-\nu}^m$). Table 1 gives the value of ν and the coefficients $\tilde{\alpha}$ and $\tilde{\beta}$ by

$$\tilde{P}s_\nu^m(\xi) = \tilde{\alpha}\tilde{F}s_\nu^m(\lambda, c\xi) + \tilde{\beta}\tilde{F}s_{-1-\nu}^m(\lambda, c\xi) \tag{27}$$

It can immediately be seen that only one term in Eq. (27) is dominant for large l. Furthermore the procedure described in Ref. [1] becomes exact for the case $|p| = |q|$, i.e. the one-centre problem in prolate spherical coordinates. (Eq. (A25) also shows that for $|p| \approx |q|$ ν is close to an integer). Thus we may conclude that Ref. [1] provides approximate solutions whenever the characteristic exponent ν is near an integer, that is for $l \gg kR$ or $|p| \approx |q|$. Such approximations should, however, be used with caution.

Acknowledgement. We would like to thank M. Gyulassy and M. Gros for several useful discussions.

Appendix

We wish to discuss certain aspects of the solution of Eq. (4) and the associated *RR*s (8, 9, 12) in greater detail. We shall be concerned with

1) The convergence of the solutions.
2) The relationship between the various solutions.
3) The numerical methods used to calculate the solutions.

A1. The Convergence of the Solutions

A1.1. The Convergence of the Recursion Relation

Let us take the *RR* (9) as an example. Similar remarks also apply to the other *RR*s (8, 12). We shall consider the situation for $|N| \gg 1$, and assume $(d^m_{\nu+N})/(d^m_{\nu+N+1}) \approx (d^m_{\nu+N+1})/(d^m_{\nu+N+2}) = x$, to order $1/N^2$. Then keeping terms of order $1/N^2$ we get from (9)

$$\frac{1}{4}C^2X^4 - N^2X^2 + \frac{1}{4}C^2 = 0 \tag{A1}$$

This has four solutions

$$x = \pm 2N/c \tag{A2a}$$

$$x = \pm c/2N \tag{A2b}$$

Thus the 5-term *RR* (9) has four independent solutions, and the general solution is a linear combination of these. Using the same conventions the 3-term *RR* (12) has two independent solutions given by

$$x = N/c \tag{A3a}$$

$$x = c/N \tag{A3b}$$

A1.2. The Convergence of the Solutions Fs^m_ν, Qs^m_ν, $\tilde{F}s^m_\nu$, Ps^m_ν, $\mathbb{P}s^m_\nu$

Considering the asymptotic form for the basis functions we have for $|N| \to \infty$

$$F_{\nu+N}(\lambda, c\xi) \to \frac{(2\pi)^{1/2}(c\xi)^{\nu+N+1}}{2^{(\nu+N+1)}[\Gamma(1+\nu+N+i\lambda)\Gamma(1+\nu+N-i\lambda)]^{1/2}} \qquad \text{for all } \xi \text{ [4]} \tag{A4}$$

$$Q^m_{\nu+N}(\xi) \to (\tfrac{1}{2}\pi)^{1/2}\frac{\Gamma(1+\nu+m+N)}{\Gamma(\frac{3}{2}+\nu+N)}(\xi^2-1)^{-1/4}[\xi-(\xi^2-1)^{1/2}]^{\nu+N+(1/2)}$$

for all ξ off the cut [3] (A5)

Therefore picking the convergent solutions for the *RR*s we have

$$\left|\frac{d^m_{\nu+N}F_{\nu+N}}{d^m_{\nu+N-1}F_{\nu+N-1}}\right| \to \frac{\xi}{N} \qquad N \to +\infty \tag{A6a}$$

$$\left|\frac{d^m_{\nu+N}F_{\nu+N}}{d^m_{\nu+N+1}F_{\nu+N+1}}\right| \to \frac{1}{\xi} \qquad N \to -\infty \tag{A6b}$$

$$\left|\frac{a^m_{\nu+N}Q^m_{\nu+N}}{a^m_{\nu+N-1}Q^m_{\nu+N-1}}\right| \to \frac{c}{2N}[\xi-(\xi^2-1)^{1/2}] \qquad N \to +\infty \tag{A6c}$$

$$\left|\frac{a^m_{\nu+N}Q^m_{\nu+N}}{a^m_{\nu+N+1}Q^m_{\nu+N+1}}\right| \to \frac{c}{2N}\,[\xi-(\xi^2-1)^{1/2}]^{-1} \qquad N\to-\infty \tag{A6d}$$

Thus the series for Fs^m_ν converges whenever $|\xi|>1$ and Qs^m_ν converges if ξ is off the cut. Similarly it can be shown that $\tilde{F}s^m_\nu$ converges whenever $|\xi+1|>2$. The convergence of Ps^m_ν follows from the convergence of Qs^m_ν. $\mathbb{P}s^m_\nu$ may similarly be shown to converge in the region $-1<\xi\leqslant+1$ either by considering its asymptotic form in this region [7], or from the convergence of Ps^m_ν.

A2. The Relationship Between the Solutions

A2.1. Another Representation of the Solution

We may derive another representation of the solution which provides an obvious link between the solutions $\tilde{F}s^m_\nu(\lambda, c\xi)$ and $Qs^m_\nu(\xi)$. We shall therefore call this solution $\tilde{Q}s^m_\nu(\xi)$. Writing

$$\tilde{Q}s^m_\nu = e^{\pm ic\xi}\sum_{n=-\infty}^{n=\infty}\tilde{a}^{(\pm)m}_{\nu+n}Q^m_{\nu+n}(\xi) \tag{A7}$$

and substituting this expression in Eq. (4) we find the RR satisfied by the $\tilde{a}^{(\pm)m}_{\nu+n}$ is

$$\tilde{V}^\pm_{n+1}\tilde{a}^{(\pm)m}_{\nu+n+1}+\tilde{U}^\pm_n\tilde{a}^{(\pm)m}_{\nu+n}+\tilde{T}^\pm_{n-1}a^{(\pm)m}_{\nu+n-1}=0 \tag{A8a}$$

with

$$\tilde{V}^\pm_{n+1}=\frac{[q\mp 2ic(\nu+n+1)](\nu+n+m+1)}{(2\nu+2n+3)} \tag{A8b}$$

$$\tilde{U}^\pm_n=(\nu+n)(\nu+n+1)+c^2-A \tag{A8c}$$

$$\tilde{T}^\pm_{n-1}=\frac{[q\pm 2ic(\nu+n)](\nu+n-m)}{(2\nu+2n-1)} \tag{A8d}$$

Clearly this RR has similar properties to Eq. (12). We may also define

$$\tilde{P}s^m_\nu = e^{\pm ic\xi}\sum_{n=-\infty}^{\infty}\tilde{a}^{(\pm)m}_{\nu+n}P^m_{\nu+n}(\xi)$$

A2.2. The Relationship Between the Solutions

We have a total of ten different representations for the solution to Eq. (4). However since only two independent solutions are possible, these representations must be related. We shall give the important relationships between the $Ps^m_\nu Qs^m_\nu$ and Fs^m_ν. First let us note that, if the substitution $\nu+n\to-\nu-1-n$ is made in any of the RR (8, 9, 12, A8) it can be seen (in conjunction with (A20)) that $a^m_{-1-\nu-n}=a^m_{\nu+n}$ if we have picked $a^m_{-1-\nu}=a^m_\nu$. Using this and the equation

$$P^m_\nu(\xi)=\frac{1}{\pi}\tan(\pi\nu)[Q^m_\nu(\xi)-Q^m_{-1-\nu}(\xi)] \tag{A9}$$

and noting $\tan(\nu+n)\pi=\tan(\pi\nu)$ we have

$$Ps^m_\nu(\xi)=\frac{1}{\pi}\tan(\pi\nu)[Qs^m_\nu(\xi)-Qs^m_{-1-\nu}(\xi)] \tag{A10a}$$

$$\tilde{P}s_\nu^m(\xi) = \frac{1}{\pi}\tan(\pi\nu)[\tilde{Q}s_\nu^m(\xi) - \tilde{Q}s_{-1-\nu}^m(\xi)] \tag{A10b}$$

The solutions $Qs_{-1-\nu}^m(\xi)$ and $Fs_\nu^m(\xi)$ have the property that

$$Qs_{-1-\nu}^m(e^{2\pi i}\xi) = e^{2\pi i\nu}Qs_{-1-\nu}^m(\xi)$$
$$Fs_\nu^m(e^{2\pi i}\xi) = e^{2\pi i\nu}Fs_\nu^m(\xi)$$

Furthermore $Fs_{-1-\nu}^m$ and Fs_ν^m are independent and therefore

$$Qs_{-1-\nu}^m(\xi) = \alpha Fs_\nu^m(\xi) + \beta Fs_{-1-\nu}^m(\xi)$$

and letting $\xi \to e^{2\pi i}\xi$ gives $Qs_{-1-\nu}^m(\xi) = \alpha Fs_\nu^m(\xi) + \beta Fs_{-1-\nu}^m(\xi)\cdot e^{4\pi i\nu}$ and assuming $\nu \neq n$ or $n + \frac{1}{2}$ we must have $\beta = 0$ and therefore

$$Qs_{-1-\nu}^m(\xi) \propto Fs_\nu^m(\xi)$$

Similarly we have $Qs_{-1-\nu}^m \propto \tilde{Q}s_{-1-\nu}^m \propto \tilde{F}s_\nu^m \propto Fs_\nu^m$. The constants of proportionality may be evaluated by expanding a hypergeometric series representation for $Q_{\nu+n}^m$ and the confluent hypergeometric representation for $F_{\nu+n}$ and comparing like terms. We give the most important relationships below. In all cases j is an arbitrary integer and $H_\nu(j)$ is independent of j.

a) $Q_{-1-\nu}^m(\xi) = H_\nu^{(a)}(j)Fs_\nu^m(\lambda, c\xi)$:

Using

$$Q_{-1-\nu}^m(\xi) = (-1)^m \frac{2^\nu\pi^{1/2}\Gamma(-\nu+m)}{\Gamma(\frac{1}{2}-\nu)}\xi^\nu\left[\frac{\xi^2-1}{\xi^2}\right]^{1/2m} \times$$
$$\times\ {}_2F_1\left(\tfrac{1}{2} - \tfrac{1}{2}\nu + \tfrac{1}{2}m, -\tfrac{1}{2}\nu + \tfrac{1}{2}m, \tfrac{1}{2} - \nu; \frac{1}{\xi^2}\right) \tag{A11}$$

we derive

$$H_\nu^{(a)}(j) = -\frac{\pi^{1/2}\cot(\pi\nu)}{c^{(1+\nu+j)}\Gamma(1+\nu+j-m)} \times$$
$$\times \frac{\displaystyle\sum_{n=0}^{\infty} a_{\nu+j+2n}^m \frac{\Gamma(\frac{1}{2}+\nu+j+n)}{n!}(-1)^n}{\displaystyle\sum_{k=0}^{\infty} d_{\nu+j-k}^m \left[\frac{\Gamma(1+\nu+j-k+i\lambda)}{\Gamma(1+\nu+j-k-i\lambda)}\right]^{1/2}(i)^k \sum_{s=0}^{k}\frac{(-\frac{1}{2})^{k-s}\Gamma(1+\nu+j+s-k-i\lambda)}{s!(k-s)!\Gamma(2\nu+2j+2-2k+s)}} \tag{A12}$$

b) $\tilde{Q}s_{-1-\nu}^m(\xi) = H_\nu^{(b)}(j)\tilde{F}s_\nu^m(\lambda, c\xi)$:

Using

$$Q_{-1-\nu}^m(\xi) = (-1)^m 2^{-1-\nu}\frac{\Gamma(-\nu)\Gamma(-\nu+m)}{\Gamma(-2\nu)}\left[\frac{\xi+1}{\xi-1}\right]^{1/2m}(\xi+1)^\nu \times$$
$$\times\, {}_2F_1\left(-\nu-m, -\nu, -2\nu; \frac{2}{1+\xi}\right) \tag{A13}$$

we derive

$$H_\nu^{(b)}(j) = -\frac{\pi}{\tan(\pi\nu)}\frac{e^{ic}(\frac{1}{2})^{2\nu+2j}c^{-(\nu+j)}}{\Gamma(1+\nu+j-i\lambda)\Gamma(1+\nu+m+j)\Gamma(1+\nu+j)}$$

$$\times\frac{\sum_{n=0}^{\infty}\tilde{a}_{\nu+n+j}^{(-)m}(-1)^n\frac{\Gamma(1+\nu+n+j+m)\Gamma(1+2\nu+2j+n)}{n!\Gamma(1+\nu+n+j-m)}}{\sum_{n=0}^{\infty}\tilde{d}_{\nu+j-n}^{m}\left[\frac{\Gamma(1+\nu+j-n+i\lambda)}{\Gamma(1+\nu+j-n-i\lambda)}\right]^{1/2}\frac{(i)^n}{n!\Gamma(2+2\nu+2j-n)}} \tag{A14}$$

c) $\tilde{Q}s_{-1-\nu}^{m}(\xi) = H_\nu^{(c)}(j)Fs_\nu^m(\lambda, c\xi)$:

Using the same representation for $Q_{-1-\nu}^{m}$ as a) we derive

$$H_\nu^{(c)}(j) = \frac{-\pi^{1/2}\cot(\pi\nu)}{\Gamma(1+\nu+j-m)\Gamma(1+\nu+j-i\lambda)}c^{-(1+\nu+j)}$$

$$\times\frac{\sum_{n=0}^{\infty}\tilde{a}_{\nu+j+2n}^{(-)m}\frac{\Gamma(\frac{1}{2}+\nu+j+n)}{n!}(-1)^n}{\sum_{n=0}^{\infty}d_{\nu+j-n}^{m}\left[\frac{\Gamma(1+\nu+j-n+i\lambda)}{\Gamma(1+\nu+j-n-i\lambda)}\right]^{1/2}\frac{(i)^n}{n!\Gamma(2\nu+2j+2-n)}} \tag{A15}$$

A3. Numerical Methods

Eq. (16) gives a relationship between ν and A defined implicitly by $\mathscr{F}(\nu, A_\nu) = 0$. However, the determination of the zeros of a function without good starting values is difficult and we shall therefore describe the methods used to generate these starting values. We shall be concerned with the two problems of determining A_ν given ν, and determining $\nu(A)$ given A.

A3.1. The Value of A_ν Given ν

Since we require the convergent solutions to the *RR* we shall assume that there exists some $N \gg 1$ so that $a_{\nu+n}^m \approx a_{\nu-n}^m \approx 0$ for all $n > N$ (taking the *RR*(8) as an example). The *RR* then gives $2N + 1$ simultaneous linear equations and the condition that these should have a non-trivial solution is obviously

$$\det(\mathbf{M}_{(\nu)}^{(N)} - A\mathbf{I}) = 0 \tag{A16}$$

where we have written the (truncated) *RR* in the form

$$\mathbf{M}_{(\nu)}^{(N)}\mathbf{a}_\nu^{(N)} = 0 \tag{A17}$$

where

$$\mathbf{a}_\nu^{(N)} = \begin{bmatrix} a_{\nu-N}^m \\ \vdots \\ a_\nu^m \\ \vdots \\ a_{\nu+N}^m \end{bmatrix} \tag{A18}$$

and

$$\mathbf{M}_{(\nu)}^{(N)} = \begin{bmatrix} u_{-N}^*, & v_{-N+1}, & w_{-N+2} & & \\ \hdashline s_{-2}, & t_{-1}, & u_0^*, & v_1, & w_2 \\ \hdashline & & s_{N-2}, & t_{N-1}, & u_N^* \end{bmatrix} \tag{A19}$$

with $u_n^* = u_n + A$, i.e. $\mathbf{M}_{(\nu)}^{(N)}$ is independent of A. Thus for a given N and ν we obtain $2N+1$ A_ν's which from (A16) are obviously the eigenvalues of $\mathbf{M}_{(\nu)}^{(N)}$. Further it is easy to show that $\mathbf{M}_{(\nu)}^{(N)}$ and $M_{(-1-\nu)}^{(N)}$ have the same eigenvalues and therefore

$$A_\nu = A_{-1-\nu} \tag{A20}$$

Two other important properties also follow from the properties of $M_{(\nu)}^{(N)}$. First by multiplying each row and column of det $(\mathbf{M}_{(\nu)}^{(N)} - A\mathbf{I})$ by (-1) it can easily be shown that the eigenvalues A are invariant under the substitution $q \to -q$. Further by letting $N \to \infty$ and making the substitution $\nu \to \nu + l$ it can be shown that the eigenvalues are invariant against this substitution. Finally, we remark that the 1 to 1 relationship between ν and A_ν defined by Eq. (16) requires that all the RR must give the same values of A for a given ν. Although this is not obvious it is indeed the case, and the computation of A_ν has been carried out by diagonalizing the matrices given by RR (8), (9) and (12). It is found that Eq. (8) gives the fastest diagonalization procedure and this is therefore used to calculate A_ν. This procedure is also applicable to the case of integral ν, in which case the matrix terminates to the upper left.

A3.2. The value of ν Given A

For this purpose we require the definition of ν as the characteristic exponent. We assume y_1 has the properties given by Eq. (5a) and write y_1 as a linear combination of the two independent solutions η_1 and η_2 which have the property that at z_0

$$\begin{aligned} &\eta_1(z_0) = 1 \qquad \eta_2(z_0) = 0 \\ &\eta_1'(z_0) = 0 \qquad \eta_2'(z_0) = 1 \\ &y_1(z_0) = a\eta_1(z_0) + b\eta_2(z_0) = a \end{aligned} \tag{A21}$$

and using the circulation property of y_1

$$y_1(e^{2\pi i}z_0) = e^{2\pi i\nu}a = a\eta_1(e^{2\pi i}z_0) + b\eta_2(e^{2\pi i}z_0) \tag{A22a}$$

Considering the derivatives we may also derive

$$e^{2\pi i\nu}b = a\eta_1'(e^{2\pi i}z_0) + b\eta_2'(e^{2\pi i}z_0) \tag{A22b}$$

The condition that these two equations in a and b have a non-trivial solution, is

$$\det \begin{bmatrix} \eta_1(e^{2\pi i}z_0) - e^{2\pi i\nu} & \eta_2(e^{2\pi i}z_0) \\ \eta_1'(e^{2\pi i}z_0) & \eta_2'(e^{2\pi i}z_0) - e^{2\pi i\nu} \end{bmatrix} = 0 \tag{A23a}$$

or

$$W(e^{2\pi i}z_0) - e^{2\pi i\nu}[\eta_1(e^{2\pi i}z_0) + \eta_2'(e^{2\pi i}z_0)] + e^{4\pi i\nu} = 0 \tag{A23b}$$

where $W(z) = \eta_1(z)\eta_2'(z) - \eta_1'(z)\eta_2(z)$ is the Wronskian, which can be shown to be of the form $K/(z^2-1)$. Using the values of $\eta_{1,2}, \eta'_{1,2}$ given above we see $K = z_0^2 - 1$ and $W(e^{2\pi i}z_0) = 1$. This gives

$$\cos(2\pi\nu) = \tfrac{1}{2}[\eta_1(e^{2\pi i}z_0) + \eta'_2(e^{2\pi i}z_0)] \tag{A24}$$

Now it is shown in Ref. [3] that $\eta_{1,2}, \eta'_{1,2}$ are entire transcendental functions of A of order $\leqslant \frac{1}{2}$ for any given z_0. Therefore, cos $2\pi\nu$ is an entire transcendental function of A and may be expanded in terms of its zeros [9]. Using arguments similar to those given in Ref. [3] (Sect. 3.53) we finally derive

$$\frac{1-\cos(2\pi\nu)}{1+\cos(\pi\sqrt{4A-2c^2+1})} = \prod_{n=-\infty}^{\infty} \frac{A-A_n(c^2)}{A-\frac{1}{2}c^2-n(n+1)} \tag{A25}$$

The values of A_n may be derived from the diagonalization of $\mathrm{M}^{(N)}_{(\nu=0)}$ and hence starting values for ν as a function of A may be obtained.

We may note that according to Eq. (25) ν is not required to be real, and indeed, in general we find complex values. Furthermore, if ν_0 is a solution to (A25) so is $-1-\nu_0$. Hence unless $\nu = n$ or $n+\frac{1}{2}$ there is another independent solution y_2 with the characteristic exponent $-1-\nu$ as in Eq. (5b). If $\nu = n$ we must have $A = A_n$. A_n is always an eigenvalue of $M_{\nu=0}$ and hence $\nu = n$ implies that Eqs. (3) and (4) generate the same eigenvalues. This is only possible if $|p| = |q|$, i.e. either Z_1 or $Z_2 = 0$. This is the one-centre case in prolate elliptical coordinates. The case $\nu = n + \frac{1}{2}$ we shall not treat further.

A3.3. The Numerical Methods

We start with the parameters which define the problem:

E	the energy of the continuum state
R	the internuclear separation
$Z_1 Z_2$	the nuclear charges
l	the asymptotic angular momentum
m	the azimuthal angular momentum

Using the variables E/Z_2^2 and Z_2R it is easy to see that the solutions scale with Z_2, and $Z = Z_1/Z_2$ is the only free charge parameter. We first calculate the parameters of the problem c, p, q, λ and determine A_l by diagonalizing $\mathrm{M}_m^{(15)}$ (with q replaced by $-p$). Diagonalizing $\mathrm{M}_0^{(14)}$ gives 29 A_n values for the calculation of ν according to Eq. (A25). The value of ν is then improved using Eq. (12) and the prescription in the text.

The solutions to the *RR* are then constructed. The 3-term *RR* present no problem, the prescription given in the text may be used. The 5-term *RR*s are solved by a method analogous to that used in Ref. [1]. Picking a large value of N(=50 in our case), we set all terms with $n > N$ or $n < -N = 0$ and iterate backwards to $n = 0$, using two different arbitrary sets of starting values. The requirement that these solutions should match in the neighborhood of $n = 0$ then generates four homogeneous simultaneous equations, three of which we solve as an ordinary problem. This gives the linear combination of solutions required. The value of the 4th expression (which should be zero if ν has been correctly calculated), is found to be less than $\approx 10^{-7}$ in most cases. The normalization is then adjusted so that the leading term $(a_\nu^m) = 1$. The overall normalization, and phase shift, have been calculated using Eqs. (A10b) and (A14) in conjunction with the asymptotic form for $F_{\nu+n}(\lambda, c(\xi+1))$.

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