Theoret. Chim. Acta (Berl.) 38, 185—197 (1975)

Non Relativistic Continuum Wave Functions for Two Coulomb Centres*

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Received March 5, 1975

We give the continuum wave function solutions to the Schrödinger equation for an electron moving in the Coulomb field of two point nuclei, as an expansion in terms of one centre Coulomb wave functions in a prolate elliptical coordinate system. These solutions may be chosen to have a convenient asymptotic behaviour, and tend to the conventional solutions of the Helmholtz equation in the limit that the nuclear charge goes to zero. In symmetric systems, where both nuclei have the same charge the angular wave functions are found to be identical with those occurring in the free case, and the expansion coefficients for the corresponding radial solutions are given for selected values of electron energy and nuclear separation.

Key word: Continuum wave functions, non-relativistic ~

1. Introduction

It is well known that the Schrödinger equation for an electron moving in the Coulomb field of two nuclei is separable in prolate elliptical coordinates [1, 2]. Several solutions for the bound states exist, and correlation diagrams of energy eigenvalues as a function of internuclear separation are available [2–4].

The Dirac equation with two Coulomb centres has also been solved for bound states and the corresponding relativistic correlation diagrams obtained [5]. Non characteristic X-rays observed in heavy ion collisions below the Coulomb barrier can be attributed to transitions between these quasimolecular levels, and for a total charge $Z(\text{target}) + Z(\text{projectile}) \approx 137$ these relativistic wave functions must be used for the deeply bound states. In order to examine the total K-shell vacancy production we wish to calculate the cross section for excitation of K electrons to low lying continuum states through the radial and Coriolis coupling described in Ref. [6]. As a first step we take advantage of the separability of the Schrödinger equation to calculate almost analytic two centre non-relativistic Coulomb wave functions which have a structure similar to the known almost analytic solutions to the Helmholtz-equation in prolate elliptical coordinates [7].

* This work was supported by the Bundesministerium für Forschung und Technologie (BMFT), and by the Gesellschaft für Schwerionenforschung (GSI).

2. Solution of the Schrödinger Equation

2.1. Separation

We work in a system of prolate elliptical coordinates (ξ, η, ϕ) defined by $\xi = \frac{r_1+r_2}{R}$; $\eta = \frac{r_1-r_2}{R}$ with ϕ the angle between the (x, z)-plane, and the plane containing r_1 and r_2 (see Fig. 1).

Thus

$$x = \tfrac{1}{2} R[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}} \cos\phi$$
$$y = \tfrac{1}{2} R[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}} \sin\phi$$
$$z = \tfrac{1}{2} R\xi\eta$$

with

$$1 \leqq \xi \leqq \infty; \quad -1 \leqq \eta \leqq +1; \quad 0 \leqq \phi < 2\pi,$$

where R is the internuclear separation.

The two nuclei have charges Z_1 and Z_2 and the potential felt by an electron at $\boldsymbol{r}$ is

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

where α measures the strength of the interaction. We work in natural units throughout, so that α is the fine structure constant.

In this coordinate system with this potential the Schrödinger equation separates to give [1, 2], for positive energy E

$$\frac{d^2\Phi}{d\Phi^2} + m^2\Phi = 0, \tag{1}$$

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

$$\frac{d}{d\xi}\left\{(\xi^2-1)\frac{dX}{d\xi}\right\} - \frac{m^2 X}{\xi^2-1} + [c^2\xi^2 + q\xi - A]X = 0, \tag{3}$$

where $p = \alpha(Z_2 - Z_1)R$; $q = \alpha(Z_1 + Z_2)R$; $c^2 = \frac{1}{2}ER^2$ and m and A are separation constants. The solution to the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}, \boldsymbol{R})\right]\Psi = E\Psi$$

is then given by the product

$$\Psi(\xi, \eta, \phi) = X(\xi)S(\eta)\Phi(\phi).$$

Equation (1) may be solved immediately to give $\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ (m integer) expressing the rotational symmetry of the problem about the z-axis. In the limit

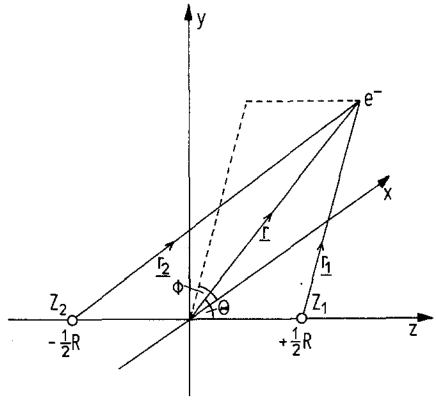

Fig. 1. The coordinate system used to describe the wave functions

$R \to 0$, $\xi \to r$ and $\eta \to \cos\theta$ (see Fig. 1). Equation (2) is therefore the two center analogue of the angular equation in the one center case, while Eq. (3) is the analogue of the radial equation. In the case $Z_1 = Z_2 = 0$ so that $p = q = 0$ these equations reduce to the separated Helmholtz equation in prolate elliptical coordinates, whose solutions are known [7]. We wish to find the solutions to (2) and (3) which reduce to these solutions in a simple and direct way as p and $q \to 0$.

2.2. The Angular Equation

The solution to the angular equation is given by Chakravarty [2] as a sum of Legendre polynomials

$$S_{ml}(c, p, \eta) = \sum_{n=0}^{\infty} d_n^{ml}(c, p) P_{m+n}^m(\eta), \tag{4}$$

where the $d_n^{ml}(c, p)$ satisfy the recursion relation (RR)

$$w_{n+2}^{ml} d_{n+2}^{ml} + v_{n+1}^{ml} d_{n+1}^{ml} + u_n^{ml} d_n^{ml} + t_{n-1}^{ml} d_{n-1}^{ml} + s_{n-2}^{ml} d_{n-2}^{ml} = 0 \tag{5}$$

with

$$w_{n+2}^{ml} = \frac{(n+2m+1)(n+2m+2)}{(2m+2n+3)(2m+2n+5)} c^2, \tag{6a}$$

$$v_{n+1}^{ml} = -\frac{(n+2m+1)}{(2m+2n+3)} p, \tag{6b}$$

$$u_n^{ml} = (m+n)(m+n+1) - A_{ml} + \frac{2(n+m)(n+m+1) - 2m^2 - 1}{(2m+2n-1)(2m+2n+3)} c^2, \tag{6c}$$

$$t_{n-1}^{ml} = \frac{-n}{(2m+2n-1)} p, \tag{6d}$$

$$s_{n-2}^{ml} = \frac{n(n-1)c^2}{(2m+2n-1)(2m+2n-3)}. \tag{6e}$$

Here A_{ml} is the separation constant, which is clearly labelled by the eigenvalue m. The RR (5) may be considered as an infinite set of homogeneous equations for the coefficients d_n^{ml}. The condition that this set should have a non trivial solution is given by considering the determinant

$$\Delta_A(c, p) = \det(\boldsymbol{M} - \boldsymbol{I}A) = 0 =$$

$$= \left| \begin{array}{cccccccccccc} - & - & - & - & - & - & - & - & - & - & - & - \\ - & 0 & s_{n-4} & t_{n-3} & \bar{u}_{n-2} - A & v_{n-1} & w_n & 0 & - & - & - & - \\ - & 0 & 0 & s_{n-3} & t_{n-2} & \bar{u}_{n-1} - A & v_n & w_{n+1} & 0 & - & - & - \\ - & 0 & 0 & 0 & s_{n-2} & t_{n-1} & \bar{u}_n - A & v_{n+1} & w_{n+2} & 0 & - & - \\ - & 0 & 0 & 0 & 0 & s_{n-1} & t_n & \bar{u}_{n+1} - A & v_{n+2} & w_{n+3} & 0 & - \\ - & - & - & - & - & - & - & - & - & - & - & - \end{array} \right| \tag{7}$$

with

$$\bar{u}_n^{ml} = (m+n)(m+n+1) + \frac{2(n+m)(n+m+1) - 2m^2 - 1}{(2m+2n-1)(2m+2n+3)} c^2 = u_n^{ml} + A_{ml}.$$

If $\Delta_A(c, p) = 0$ then there is a non-trivial solution for the d_n^{ml}. Hence the A_{ml} are the eigenvalues of $\boldsymbol{M}$, labelled by $l = m + k$, $k = 0, 1, 2, \ldots$. The convergence of $\Delta_A(c, p)$ and the calculation of the eigenvalues A_{ml} are discussed in Refs. [2, 7]. It should be noticed that as $p \to 0$ the RR 5 and eigenvalues matrix 7 reduce to the free particle RR and eigenvalue problem, discussed in Ref. [7]. Thus for symmetric systems ($Z_1 = Z_2$) the angular solutions are identical to the free particle angular solutions. We shall return to the calculation of the d_n^{ml} in Section 3.

2.3. *The Radial Equation*

In the free case, $q = 0$, we know the solutions to the radial Eq. (3) may be written

$$X_{ml}(c, q=0, \xi) \propto \frac{1}{c\xi}\left(\frac{\xi^2 - 1}{\xi^2}\right)^{m/2} \sum_{\substack{n\,\mathrm{even}=0 \\ n\,\mathrm{odd}=1}}^{\infty} i^{n+m-l} \frac{(2m+n)!}{n!} \begin{cases} c\xi j_{m+n}(c\xi) \\ c\xi y_{m+n}(c\xi) \end{cases} \tag{8a}$$

with the asymptotic form

$$X_{ml}(c, q=0, \xi) \xrightarrow[c\xi \to \infty]{} \begin{cases} j_l(c\xi) \\ y_l(c\xi), \end{cases} \tag{8b}$$

where $j_\nu(c\xi)$, $y_\nu(c\xi)$ are spherical Bessel functions of the 1st and 2nd kind. For the two center Coulomb problem we seek analogous solutions in terms of the usual one center Coulomb wave functions [9].

Putting

$$X(c, q, \xi) = \frac{1}{\xi}\left(\frac{\xi^2 - 1}{\xi^2}\right)^{m/2} Y(c, q, \xi) \tag{9}$$

gives, with $c\xi = x$

$$x^2 \frac{d^2 Y}{dx^2} + \left[x^2 + \frac{q}{c} x - A_{ml}\right] Y - c^2 \left\{\frac{d^2 Y}{dx^2} - \frac{2(m+1)}{x}\frac{dY}{dx} + \frac{(m+1)(m+2)}{x^2} Y\right\}$$
$$= GY = 0 \tag{10}$$

for the equation satisfied by Y.

Let us compare this with the Coulomb wave equation

$$\frac{d^2U_L(x)}{dx^2}+\left[1-\frac{2\eta}{x}-\frac{L(L+1)}{x^2}\right]U_L(x)=\mathscr{F}_L U_L(x)=0\,. \tag{11}$$

If we consider $H_L U_L=(G-\mathscr{F}_L)U_L$ then we get, putting $\eta=-\frac{1}{2}q/c$

$$H_L U_L=\left\{[L(L+1)-A_{ml}]-c^2\left[\frac{d^2}{dx^2}+\frac{2(m+1)}{x}\frac{d}{dx}-\frac{(m+1)(m+2)}{x^2}\right]\right\}U_L \tag{12}$$

and using the RR for the Coulomb wave functions [9] we may write

$$H_L U_L=\textstyle\sum_{\mu=-2}^{\mu=2} a_{LL+\mu}U_{L+\mu} \tag{13}$$

with

$$a_{LL+2}=-\frac{(L+m+1)(L+m+2)[(L+1)^2+\eta^2]^{\frac{1}{2}}[(L+2)^2+\eta^2]^{\frac{1}{2}}}{(L+1)(L+2)(2L+1)(2L+3)}c^2\,, \tag{14a}$$

$$a_{LL+1}=\frac{2m\eta[(L+1)^2+\eta^2]^{\frac{1}{2}}(L+m+1)}{L(L+1)(L+2)(2L+1)}c^2\,, \tag{14b}$$

$$a_{LL}=L(L+1)-A_{ml}+c^2\left\{\frac{2L(L+1)-2m^2-1}{2(L-1)(2L+3)}+2\eta^2\frac{[L(L+1)-3m^2]}{L(L+1)(2L-1)(2L+3)}\right\}, \tag{14c}$$

$$a_{LL-1}=\frac{-2\eta m[L^2+\eta^2]^{\frac{1}{2}}}{(L-1)L(L+1)(2L+1)}(L-m)c^2\,, \tag{14d}$$

$$a_{LL-2}=\frac{-[L^2+\eta^2]^{\frac{1}{2}}[(L-1)^2+\eta^2]^{\frac{1}{2}}}{(L-1)L(2L-1)(2L+1)}(L-m)(L-m-1)c^2\,. \tag{14e}$$

Now if $(G-\mathscr{F}_L)U_L=\sum_\lambda a_{L\lambda}U_\lambda$ then $Y=\sum_\nu f_\nu U_\nu$ is a solution of $GY=0$ if the f_ν satisfy the RR (see Ref. [10])

$$\textstyle\sum_\lambda a_{\lambda\mu}f_\lambda=0 \tag{15}$$

that is, the RR satisfied by the f_λ is

$$\tilde{w}^{ml}_{n+2}f^{ml}_{n+2}+\tilde{v}^{ml}_{n+1}f^{ml}_{n+1}+\tilde{u}^{ml}_{n}f^{ml}_{n}+\tilde{t}^{ml}_{n+1}f^{ml}_{n-1}+\tilde{s}^{ml}_{n-2}f^{ml}_{n-2}=0 \tag{16}$$

with

$$\tilde{w}^{ml}_{n+2}=-\frac{[(m+n+2)^2+\eta^2]^{\frac{1}{2}}[(m+n+1)^2+\eta^2]^{\frac{1}{2}}(n+1)(n+2)}{(m+n+1)(m+n+2)(2m+2n+3)(2m+2n+5)}c^2\,, \tag{17a}$$

$$\tilde{v}^{ml}_{n+1}=-\frac{2\eta m[(m+n+1)^2+n^2]^{\frac{1}{2}}(n+1)}{(n+m)(n+m+1)(n+m+2)(2n+2m+3)}c^2\,, \tag{17b}$$

$$\tilde{u}^{ml}_{n}=(m+n)(m+n+1)-A_{ml}+c^2\left\{\frac{2(m+n)(m+n+1)-2m^2-1}{(2m+2n-1)(2m+2n+3)}\right.$$
$$\left.+\frac{2\eta^2[(m+n)(m+n+1)-3m^2]}{(m+n)(m+n+1)(2m+2n-1)(2m+2n+3)}\right\}, \tag{17c}$$

$$\tilde{t}^{ml}_{n-1}=\frac{2m\eta[(m+n)^2+\eta^2]^{\frac{1}{2}}(2m+n)}{(m+n-1)(m+n)(m+n+1)(2m+2n-1)}c^2\,, \tag{17d}$$

$$\tilde{s}^{ml}_{n-2}=-\frac{(2m+n-1)(2m+n)[(m+n-1)^2+\eta^2]^{\frac{1}{2}}[(m+n)^2+\eta^2]^{\frac{1}{2}}}{(m+n-1)(m+n)(2m+2n-3)(2m+2n-1)}c^2\,, \tag{17e}$$

where we have put $L=m+n$ (see Appendix). The f coefficients are clearly functions of c and η although this has not been explicitly indicated. It will also be convenient to define g_n^{ml} such that

$$f_n^{ml}=(i)^{n+m-l}\frac{(2m+n)!}{n!}g_n^{ml}. \tag{18}$$

The g_n^{ml} then satisfy the RR

$$w'^{ml}_{n+2}g^{ml}_{n+2}+v'^{ml}_{n+1}g^{ml}_{n+1}+u'^{ml}_n g^{ml}_n+t'^{ml}_{n-1}g^{ml}_{n-1}+s'^{ml}_{n-2}g^{ml}_{n-2}=0 \tag{19}$$

with

$$w'^{ml}_{n+2}=\frac{(2m+n+1)(2m+n+2)[(m+n+2)^2+\eta^2]^{\frac{1}{2}}[(m+n+n+1)^2+\eta^2]^{\frac{1}{2}}}{(m+n+1)(m+n+2)(2m+2n+3)(2m+2n+5)}c^2, \tag{20a}$$

$$v'^{ml}_{n+1}=-2i\eta c^2\frac{m(2m+n+1)[(m+n+1)^2+\eta^2]^{\frac{1}{2}}}{(m+n)(m+n+1)(m+n+2)(2m+2n+3)}, \tag{20b}$$

$$u'^{ml}_n=(m+n)(m+n+1)-A_{ml}+c^2\left\{\frac{2(m+n)(m+n+1)-2m^2-1}{(2m+2n-1)(2m+2n+3)}\right.$$
$$\left.+\frac{2\eta^2[(m+n)(m+n+1)-3m^2]}{(m+n)(m+n+1)(2m+2n-1)(2m+2n+3)}\right\}, \tag{20c}$$

$$t'^{ml}_{n-1}=-2i\eta c^2\frac{mn[(m+n)^2+\eta^2]^{\frac{1}{2}}}{(m+n-1)(m+n)(m+n+1)(2m+2n-1)}, \tag{20d}$$

$$s'^{ml}_{n-2}=\frac{n(n-1)[(m+n-1)^2+\eta^2]^{\frac{1}{2}}[(m+n)^2+\eta^2]^{\frac{1}{2}}}{(m+n-1)(m+n)(2m+2n-3)(2m+2n-1)}c^2. \tag{20e}$$

These equations are the analogue to the free radial equation RR, which may be recovered by letting $\eta\to 0$. We may note in passing that the pure imaginary terms in Eq. (20) give no trouble, every g_n^{ml} calculated from Eq. (20) in either pure real or pure imaginary. All the f_n^{ml} are real.

3. Convergence of the Series Solutions and Normalization

3.1. Convergence

We shall examine the convergence of the series determined by the g_n^{ml}. Exactly analogous remarks would apply to the series determined by the d_n^{ml} defined in Eqs. (5) and (6). For large n we have $(n \gg m, l, \eta)$

$$w'^{ml}_{n+2}\sim \tfrac{1}{4}c^2;\quad v'^{ml}_{n+1}\sim -i\eta c^2 m/n^2;$$
$$u'^{ml}_n\sim n^2;\quad t'^{ml}_{n-1}\sim -i\eta c^2 m/n^2;\quad s'^{ml}_{n-2}\sim \tfrac{1}{4}c^2.$$

Now using Eq. (19) we may derive

$$\frac{g^{ml}_{n+1}}{g^{ml}_{n+2}}=\cfrac{1}{\dfrac{4i\eta m}{n^2}-\dfrac{4c^2n^2g^{ml}_n}{g^{ml}_{n+1}}+\dfrac{4i\eta m}{n^2}\dfrac{g^{ml}_{n-1}}{g^{ml}_{n+1}}-\dfrac{g^{ml}_{n-2}}{g^{ml}_{n+1}}} \tag{21}$$

and if we assume $\frac{g_{n+1}^{ml}}{g_{n+2}^{ml}} \sim \gamma n^{\alpha}$ for large n we have

$$n^{\alpha-2} = \frac{1}{\frac{4i\eta m}{\gamma} - \frac{4c^2 n^{\alpha+4}}{\gamma^2} + \frac{4i\eta m n^{2\alpha}}{\gamma^3} - \frac{n^{3\alpha+2}}{\gamma^4}} \tag{22}$$

and it can be seen that $\alpha = -1$, $\gamma = 2ic$ provides a solution for large n. Similarly we could also derive

$$\frac{g_{n-1}^{ml}}{g_{n-2}^{ml}} = \frac{n^2}{4i\eta m - 4c^2 n^2 \frac{g_n^{ml}}{g_{n-1}^{ml}} + 4i\eta m \frac{g_{n+1}^{ml}}{g_{n-1}^{ml}} - \frac{g_{n+2}^{ml}}{g_{n-1}^{ml}} n^2} \tag{23}$$

and with the assumption that

$$\frac{g_{n-1}^{ml}}{g_{n-2}^{ml}} \sim \gamma n^{\alpha}$$

we reproduce Eq. (22), and hence once more require $\alpha = -1$, $\gamma = 2ic$.

Thus there are two possible solutions to the RR (19) which give for large n

$$g_n^{ml} \sim (2ic)^{-n} n!\,, \tag{24a}$$

$$g_n^{ml} \sim \left(\frac{1}{2ic}\right)^{-n} \frac{1}{n!}\,. \tag{24b}$$

Clearly (24b) provides the convergent series for $X_{ml}(c, q, \xi)$. Exactly analogous remarks apply to the series for S_{ml} generated by the d_n^{ml}. Knowing the asymptotic form of the g_n^{ml} and d_n^{ml} we may now consider solutions to the Schrödinger equation with the appropriate asymptotic normalization.

3.2. Normalization

Inspection of Eqs. (5) and (19) shows that in the general case there are two arbitrary constants ar our disposal, viz. d_0^{ml} and d_1^{ml} for the angular solutions and g_0^{ml} and g_1^{ml} for the radial solutions. Those are specified by the normalization conditions. We consider the radial solutions first.

3.2.1. Radial Part

It is convenient to discuss the normalization in terms of the f_n^{ml} [see Eqs. (16)–(18)]. We shall require that as $c\xi \to \infty\, X_{ml} \to \frac{1}{c\xi}\, U_l(c\xi)$ i.e.

$$\textstyle\sum_{n=0}^{\infty} f_n^{ml} F_{m+n}(c\xi) \to c F_l(c\xi)\,, \tag{25a}$$

$$\textstyle\sum_{n=0}^{\infty} f_n^{ml} G_{m+n}(c\xi) \to c G_l(c\xi)\,, \tag{25b}$$

where $F_{m+n}(c\xi)$, $G_{m+n}(c\xi)$ are the regular and irregular Coulomb wave functions [9]. Using the asymptotic form for these wave functions we may reduce Eq. (25) to the following conditions on the f_n^{ml}

$$\sum_{n=0}^{\infty} f_n^{ml} \cos(\phi_{m+n} - \phi_l) = c\,, \tag{26a}$$

$$\sum_{n=0}^{\infty} f_n^{ml} \sin(\phi_{m+n} - \phi_l) = 0\,, \tag{26b}$$

where

$$\phi_L = \sigma_L - \frac{L\pi}{2}\,, \tag{26c}$$

$$\sigma_L = \arg\Gamma(L+1+i\eta) = \sigma_{L-1} + \arctan\frac{\eta}{L}\,, \tag{26d}$$

i.e. σ_L is the Coulomb phase shift.

3.2.2. Angular Part

The analogous condition here is a generalization of the Stratton-Morse-Chu-Little-Corbató-scheme [7], which has the effect that for $p=0$

$$S_{ml}(c, p, \eta) \to P_l^m(\eta) \quad \text{as} \quad \eta \to 1\,. \tag{27}$$

For the case $p \neq 0$ we shall require the two conditions

$$S_{ml}(c, p, \eta) \to P_l^m(\eta) \quad \text{as} \quad \eta \to 1\,, \tag{28a}$$

$$S_{ml}(c, p, -\eta) \to P_l^m(-\eta) \quad \text{as} \quad -\eta \to 1\,, \tag{28b}$$

i.e.

$$\sum_{n=0}^{\infty} d_n^{ml} \left[\frac{(n+2m)!}{n!}\right] = \frac{(l+m)!}{(l-m)!}\,, \tag{29a}$$

$$\sum_{n=0}^{\infty} d_n^{ml} \left[\frac{(n+2m)!}{n!}\right] (-1)^{n+m} = (-1)^l \frac{(l+m)!}{(l-m)!}\,, \tag{29b}$$

or

$$\sum_{n=0}^{\infty} \chi(n, m, l) d_n^{ml} = 1\,, \tag{29c}$$

$$\sum_{n=0}^{\infty} \omega(n, m, l) d_n^{ml} = 0\,, \tag{29d}$$

with

$$\chi(n, m, l) = \frac{1}{2} \frac{(l-m)!}{(l+m)!} \frac{(2m+n)!}{n!} [1 + (-1)^{n+m-l}]\,, \tag{30a}$$

$$\omega(n, m, l) = \frac{1}{2} \frac{(l-m)!}{(l+m)!} \frac{(2m+n)!}{n!} [1 - (-1)^{n+m-l}]\,. \tag{30b}$$

3.2.3. The Calculation of the Coefficients d_n^{ml}, f_n^{ml}

In principle the coefficients may be calculated by a simple procedure which we shall describe for the f_n^{ml}. The d_n^{ml} may be calculated in an exactly analogous fashion. We shall drop the label *ml* on f_n^{ml} since it plays no role in this discussion.

Since the RR (16) is homogeneous if the set $\{f_n\}$ is a solution then so is the set $\{\alpha f_n\}$. Let us therefore pick arbitrary starting values $f_0^{(1)}$ and $f_1^{(1)}$. This enables us to calculate the set $\{f_n^1\}$ where we choose the convergent solution (24b). Similarly by choosing the starting values $f_0^{(2)}$ and $f_1^{(2)}$ we may generate another solution $\{f_n^{(2)}\}$. The required solution is then a linear combination of these two, so that defining

$$C_\nu = \sum_{n=0}^{\infty} \cos(\phi_{m+n} - \phi_l) f_n^{(\nu)}, \tag{31a}$$

$$S_\nu = \sum_{n=0}^{\infty} \sin(\phi_{m+n} - \phi_l) f_n^{(\nu)}, \tag{31b}$$

we have

$$\alpha C_1 + \beta C_2 = c, \tag{32a}$$

$$\alpha S_1 + \beta S_2 = 0, \tag{32b}$$

$$f_n = \alpha f_n^{(1)} + \beta f_n^{(2)}. \tag{32c}$$

Since $|\sin\theta| \leqq 1$, $|\cos\theta| \leqq 1$, and since the f_n are strongly convergent we may expect that only a few terms in the sums 31 will yield an accurate result and thus C_ν and S_ν may be calculated easily. The only difficulty occurs if $\Delta = \det\begin{pmatrix} C_1 & C_2 \\ S_1 & S_2 \end{pmatrix} = 0$, when the Eq. (32) become singular. It is shown in appendix one that this can only occur if

$$f_0^{(1)}/f_1^{(1)} = f_0^{(2)}/f_1^{(2)}$$

or if $\eta \to \infty$.

Consequently if we avoid these conditions the f_n may be calculated uniquely. The analogous procedure for the RR (5) yields values for the d_n^{ml}. In practice the f_n and d_n must be calculated by backward recursion since the required series decreases very rapidly in the forward direction [11]. That is to say we specify $f_N^{(\nu)}$ and $f_{N-1}^{(\nu)}$ for some large N and iterate Eq. (17) to $f_0^{(\nu)}$ with the assumption that $f_{n>N}^{(\nu)} = 0$. The $f_n^{(\nu)}$ are then normalized so that $f_0^{(\nu)} = 1$ and the appropriate linear combination calculated from Eq. (32). Values of the $f_n^{ml}(c, \eta)$ are given in Table 1 for selected values of the parameters.

Writing the overall solution as

$$\begin{aligned} \Psi_{ml}(r, E) = N X_{ml} S_{nl} \Phi_{ml} = \frac{N}{\xi}\left[\frac{\xi^2-1}{\xi^2}\right]^{\frac{1}{2}m} &\left\{\sum_{n=0}^{\infty} f_n^{ml}[F_{m+n}(c\xi) + iG_{m+n}(c\xi]\right\} \\ &\cdot \left\{\sum_{n=0}^{\infty} d_n^{ml} P_{m+n}^m(\eta)\right\} e^{im\phi}/\sqrt{2\pi} \end{aligned} \tag{33}$$

$$\frac{R^3}{8}\int_{-1}^{1} d\eta \int_0^{2\pi} d\phi (\xi^2 - \eta^2)|\Psi|^2 \to 1 \quad \text{as} \quad c\xi \to \infty$$

or

$$N = \frac{2}{R^{\frac{3}{2}} c}\left\{\sum_{n=0}^{\infty} \frac{(2m+n)!}{(2n+1)n!} |d_n^{ml}|^2\right\}^{-\frac{1}{2}}. \tag{34}$$

Table 1. Selected values of the coefficients $f_n^{ml}(\eta, R)$ [Eq. (33)] for symmetric systems with total charge $2Z$. Energies are measured in terms of $\frac{1}{8}(\alpha Z)^2 = \frac{1}{4}$ the separated atom is binding, distances in units of $1/(\alpha Z)$ the separated atom 1s Bohr radius. Negligible coefficients are set equal to zero. The notation used is $A(B) = A \cdot 10^{-B}$

$E=0.01$ $\eta=-40$ $m=0$

	$R=0.1$	$c=2.5(3)$		$R=1.0$	$c=2.5(2)$		$R=8.0$ $c=0.2$		
$n \backslash l$	0	1	2	0	1	2	0	1	2
0	2.5028(3)	−8.35(6)	1.2472(3)	2.7955(2)	−9.47(4)	1.2621(2)	−1.1144	0.4741	0.2235
1	4.17(6)	2.4990(3)	3.1200(3)	4.46(3)	2.3818(2)	3.1632(2)	−2.6702	1.3165	0.6101
2	1.39(6)	0	4.3719(3)	1.53(3)	7.72(5)	4.4259(2)	−1.9816	1.0055	0.7994
3	0	1.67(7)	3.48(7)	2.47(5)	1.59(4)	3.50(4)	−0.7714	0.4400	0.2964
4	0	0	0	2.2(6)	0	0	−0.1686	9.43(2)	9.41(2)
5	0	0	0	0	0	0	−2.55(2)	1.56(2)	1.21(2)
6		0	0	0	0	0	−2.59(3)	1.52(3)	1.69(3)
7	0	0	0	0	0	0	−2.07(4)	1.31(4)	1.10(4)

$R=2$ $l=0$

	$E=0.05$	$c=0.1118$		$E=0.1$	$c=0.1581$	
$n \backslash m$	0	1	2	0	1	2
0	0.1748	0.1208	7.6160(2)	0.2503	0.1721	0.1086
1	9.796(2)	1.610(2)	−3.4212(2)	0.1416	2.334(2)	−4.885(2)
2	3.642(2)	6.84(3)	1.0283(3)	5.307(2)	1.005(2)	1.547(3)
3	2.16(3)	2.11(4)	1.951(4)	3.22(3)	3.20(4)	−2.98(4)
4	4.8(6)	2.5(5)	2.02(6)	3.25(4)	3.9(5)	3.35(6)
5	0	0	1.1(9)	7.6(6)	5.6(7)	−3.59(7)

$R=1$ $E=0.5$ $m=0$ $c=0.17678$

$n \backslash l$	0	1	2	3	4
0	0.19836	−6.846(3)	7.998(3)	0.18687	−0.61765
1	3.2118(2)	0.16856	0.20675	0.10038	−0.47734
2	1.1674(2)	−6.006(4)	0.30173	−1.1364(2)	1.5912(2)
3	2.134(4)	1.344(3)	2.738(3)	0.18088	4.803(3)
4	2.306(5)	−1.320(6)	8.522(4)	−5.609(5)	2.4278(2)
5	1.8(7)	−1.245(6)	2.96(6)	2.604(4)	1.244(5)
6	1.0(8)	0	4.7(7)	−3.7(8)	2.168(5)

We have used the asymptotic form for X_{ml} given in Eq. (24) and the volume element in this coordinate system, given by

$$d\tau = \frac{R^3}{8}(\xi^2 - \eta^2)d\xi d\eta d\phi .$$

This normalization then corresponds to a density of one particle per unit volume at large distances ($r \gg R$).

4. Summary

In conclusion, we have constructed continuum solutions to the Schrödinger equation for the Coulomb field of two point nuclei, normalized to one particle per unit volume at large distances. These solutions have a close analogy to the solutions to the Helmholtz equation in prolate elliptical coordinates and for symmetric systems the angular equation reduces to the free particle angular equation. Table 1 shows that in many cases only a few terms in the series expansion are required to ensure good accuracy, and hence the solutions have practical utility.

Acknowledgements. I should like to thank Prof. W. Greiner for suggesting this problem. I have enjoyed useful conversations on the subject with Prof. Greiner and Dr. K. Smith. The coefficients in Table 1 were calculated at the GSI Rechenzentrum, and I would like to thank the staff there for their help, especially Frau B. Lasitschka.

Appendix I

1. Lowest Term in the Expansion of the Radial Wave Function

We wish to show that the lowest term in the expansion of Y_{ml} is the term U_m, i.e.

$$Y_{ml}=\sum_{n=0}^{\infty} U_{m+n} f_n^{ml} \tag{A1}$$

and that no terms with $n<0$ are required. This may be seen by considering Eqs. (13) and (14). Since $H_L=G_L-\mathscr{F}_L$ and $\mathscr{F}_L U_L=0$ we have

$$\begin{aligned}
GU_m&=H_m U_m=a_{m,m}U_m+\dots\\
GU_{m+1}&=H_{m+1}U_{m+1}=a_{m+1,m}U_m+\dots\\
GU_{m+2}&=H_{m+2}U_{m+2}=a_{m+2,m}U_m+\dots\\
GU_{m+3}&=H_{m+3}U_{m+3}=a_{m+3,m+1}U_{m+1}+\dots
\end{aligned}$$

since $a_{m,m-2}=a_{m,m-1}=a_{m+1,m-1}=0$. Therefore GU_{m+n} can generate no terms of order less than m whenever $n\geqq 0$. Thus the series for Y_{ml} contains no terms of order less than m and the sum in (A1) runs from $n=0\to n=\infty$.

2. The Singularities of Δ

$$\text{Suppose } \Delta=\det\begin{pmatrix} C_1 & C_2\\ S_1 & S_2\end{pmatrix}=0\,. \tag{A2}$$

Let us further suppose that the sums in Eq. (31) have been truncated at N terms so that

$$C_\nu=\sum_{n=0}^{N} f_n^{(\nu)}\cos(\phi_{m+n}-\phi_l)\,, \tag{A3a}$$

$$S_\nu=\sum_{n=0}^{N} f_n^{(\nu)}\sin(\phi_{m+n}-\phi_l)\,. \tag{A3b}$$

We also have N–2 homogeneous equations from the RR for the f_n (it is easier to see this by considering the RR for the g_n), i.e.

$$\left.\begin{aligned}
u_0' g_0^{(\nu)}+v_1' g_1^{(\nu)}+w_2' g_2^{(\nu)}&=0\\
t_0' g_0^{(\nu)}+u_1' g_1^{(\nu)}+v_2' g_2^{(\nu)}+w_3' g_3^{(\nu)}&=0\\
\dots\dots\dots\dots\dots\dots\dots\dots&
\end{aligned}\right\}\begin{array}{l}N\text{–}2\\ \text{equations}\end{array} \tag{A3c}$$

$\Delta=0$ gives two possible cases

(1) $C_1=\gamma S_1$; $C_2=\gamma S_2$

i.e.

$$\textstyle\sum_{n=0}^{N} f_n^{(1)}[\cos(\phi_{m+n}-\phi_l)-\gamma\sin(\phi_{m+n}-\phi_l)]=0\,, \tag{A4a}$$

$$\textstyle\sum_{n=0}^{N} f_n^{(2)}[\cos(\phi_{m+n}-\phi_l)-\gamma\sin(\phi_{m+n}-\phi_l)]=0\,. \tag{A4b}$$

Now the RR Eq. (A3c) taken with (A4a) give N–1 homogeneous equations in N variables. Hence they may be solved to within a normalization to give $\{f_n^{(1)}\}$. However (A3c) taken with (A4a) give exactly the same N–1 homogeneous equations whose solution can only differ from $\{f_n^{(1)}\}$ by a normalization, and hence

$$f_n^{(1)}=\varepsilon f_n^{(2)} \tag{A5}$$

Thus if $C_1=\gamma S_1$, $C_2=\gamma S_2$ then $f_n^{(1)}=\varepsilon f_n^{(2)}$ for all n. This can always be avoided by choosing $f_0^{(\nu)}$ and $f_1^{(\nu)}$ such that

$$f_0^{(1)}/f_1^{(1)}\neq f_0^{(2)}/f_1^{(2)}\,. \tag{A6}$$

(2) $C_1=\gamma C_2$; $\quad S_1=\gamma S_2$.

In this case we have the N–2 Eq. (A3c) and the two equations

$$\textstyle\sum_{n=0}^{N}(f_n^{(1)}-\gamma f_n^{(2)})\cos(\phi_{m+n}-\phi_l)=0\,, \tag{A7a}$$

$$\textstyle\sum_{n=0}^{N}(f_n^{(1)}-\gamma f_n^{(2)})\sin(\phi_{m+n}-\phi_l)=0\,. \tag{A7b}$$

This implies either $f_n^{(1)}=\gamma f_n^{(2)}$ which we may reject if (A6) is satisfied, or there exists a solution $f_n^{H}=f_n^{(1)}-\gamma f_n^{(2)}$ which satisfies the N homogeneous Eqs. (A3c) and (A7). This is only possible if

$$\det S=\det\begin{pmatrix} \cos(\phi_m-\phi_l) & \cos(\phi_{m+1}-\phi_l) & - & - \\ \sin(\phi_m-\phi_l) & \sin(\phi_{m+1}-\phi_l) & - & - \\ i^{m-l}(2m)!u_0' & i^{m-l+1}(2m+1)!v_1' & - & - \\ i^{m-l}(2m)!t_0' & i^{m-l+1}(2m+1)!u_1' & - & - \\ - & - & - & - \\ - & - & - & - \end{pmatrix}=0\,. \tag{A8}$$

Let us write $\{f_n^H\}$ as a column vector $\boldsymbol{f}^H$. Then (A8) implies $\boldsymbol{f}^H$ is an eigenvalue of $\boldsymbol{S}$ with eigenvalue 0. However since $\boldsymbol{f}^H$ satisfies the RR which may be written in matrix form we know $\boldsymbol{f}^H$ is an eigenvalue of $\boldsymbol{S}'$ with eigenvalue 1, where

$$\boldsymbol{S}'=\begin{pmatrix} 1 & 0 & - & - \\ 0 & 1 & - & - \\ i^{m-l}(2m)!u_0' & i^{m-l+1}(2m+1)!v_1' & - & - \\ i^{m-l}(2m)!t_0' & i^{m-l+1}(2m+1)!u_1' & - & - \\ - & - & - & - \\ - & - & - & - \end{pmatrix}.$$

Thus

$$\boldsymbol{S}''\boldsymbol{f}^H=(\boldsymbol{S}-\boldsymbol{S}')\boldsymbol{f}^H=-\boldsymbol{f}^H=\begin{pmatrix} \cos(\phi_m-\phi_l)-1 & \cos(\phi_{m+1}-\phi_l) & \cos\ldots & - \\ \sin(\phi_m-\phi_l) & \sin(\phi_{m+1}-\phi_l)-1 & \sin\ldots & - \\ 0 & 0 & 0 & - \\ 0 & 0 & 0 & - \\ 0 & 0 & 0 & - \\ - & - & - & - \end{pmatrix}\boldsymbol{f}^H$$

or $\boldsymbol{S}''$ must have an eigenvalue -1 and therefore

$$\det\begin{pmatrix} \cos(\phi_m-\phi_l) & \cos(\phi_{m+1}-\phi_l) & \cos\ldots & \ldots & - \\ \sin(\phi_m-\phi_l) & \sin(\phi_{m+1}-\phi_l) & \sin\ldots & \ldots & - \\ 0 & 0 & +1 & - & - \\ 0 & 0 & 0 & +1 & - \\ - & - & - & - & - \end{pmatrix}=0$$

which is only possible if

$$\tan(\phi_m - \phi_l) = \tan(\phi_{m+1} - \phi_l)$$

and from the definition of ϕ_L this is only possible if

$$\arctan\frac{\eta}{m+1} = \frac{\pi}{2}, \text{ i.e. } \eta \to \infty.$$

It is easy to show, by the same technique, that provided

$$d_0^{(1)}/d_1^{(1)} \neq d_0^{(2)}/d_1^{(2)}$$

then there is no singularity in calculating the d_n^{ml}.

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