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Continuum Wave Functions for the Two-Center, One-Electron System*

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Electronic continuum wavefunctions for the one-electron two-center system have been calculated for nuclear charges $Z_B = 1.0$, $1.0 \leqslant Z_A \leqslant 2.0$ ("near-symmetric" systems). Using scaling laws, the results for noninteger Z_A can be applied to larger bare-nucleus systems. Representative examples of computed separation constants and phase shifts are presented.

A. INTRODUCTION

Electronic continuum states for the two-center one-electron system have received little attention, although the problem is a separable one. Solutions for H_2^+ were computed by Bates *et al.* [1] in connection with photoionization of the molecule-ion. Cayford *et al.* [2] report a solution using the finite difference method. An *incorrect* solution for arbitrary charges has been reported by Greenland [3]. Ponomarev and Somov [4] have described a correct solution and present results for HeH^{2+} in particular.

Here we present an alternative to the method of Ponomarev and Somov [4] which agrees with their results but not with those of Greenland [3]. We have used it to compute continuum wavefunctions for systems with nuclear charges $Z_B = +1.0$, $+1.0 \leqslant Z_A \leqslant +2.0$ (using scaling laws, the results for nonintegral but rational (Z_A/Z_B) can be applied to larger bare-nucleus systems). Computation of these continuum states is needed for studies of direct impact ionization similar to those done earlier in this laboratory [5–7]; we have also used them to study the problem of electron translation factor corrections in slow collisions in work reported elsewhere [8].

Where possible, we have omitted details since most features of the correct solutions are given by Ponomarev and Somov [4], but we have shown some interesting aspects of phase shift behavior in the figures. Copies of the FORTRAN IV computer algorithms used to generate solutions are available upon request.

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B. SOLUTION

For a single electron in the field of two Coulombic centers $+Z_Ae$, $+Z_Be$, the solution is separable in prolate spheroidal coordinates $(\xi, \eta, \phi)(1 \leqslant \xi < \infty; -1 \leqslant \eta \leqslant +1; 0 \leqslant \phi < 2\pi)$ and may be written

$$\Psi = (2\pi)^{-1/2} X(\xi) S(\eta) \exp(im\phi). \tag{1}$$

For positive energies ϵ the "angular" and "radial" equations are, resp.,

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

and

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

where the parameters p, q, c^2 are defined

$$p = R(Z_B - Z_A), \qquad q = R(Z_A + Z_B), \qquad c^2 = \epsilon R^2/4; \tag{4}$$

R is the internuclear distance in a.u., ϵ is the energy in *Rydbergs*, and we take c to be nonnegative. A and m are separation constants; in the united atom limit ($R \to 0$), Eq. (2) tends to the equation for the associated Legendre function $P_L^{|m|}(\eta)$ with $A = L(L+1)$, and Eq. (3) becomes the radial equation for the spherical Coulomb wavefunction [9].

1. *Solution of Angular Equation*

Solutions to (2) are required which are regular in the interval $-1 \leqslant \eta \leqslant +1$. Basing our approach on the formal analogy with the equation for $\epsilon < 0$, we write

$$S(\eta) = \exp[-ic\eta] \sum_{l=|m|} d_l P_l^{|m|}(\eta) \tag{5}$$

which leads to a three-term recursion relation for the d_l's,

$$\begin{aligned}[(p + 2icl)(l - |m|)/(2l-1)]\, d_{l-1} + [A - c^2 - l(l+1)]\, d_l \\ + \{[p - 2ic(l+1)](l + |m| + 1)/(2l+3)\}\, d_{l+1} = 0,\end{aligned} \tag{6}$$

with $d_{|m|-1} = 0$. The eigenvalues A are *real* (as Ponomarev and Somov [4] point out, they depend only on absolute values of the complex coefficients in (6)) and can be determined rapidly by the usual techniques for codiagonal matrices.

The expansion (5) is not a convenient representation of the corresponding *wavefunction*; convergence is poor even for moderate values of c [4], and evaluation of matrix elements for even simple operators linking bound and continuum states is messy. We have chosen to represent the wavefunction as

$$S(\eta) = \sum_{l=|m|} d_l' P_l^{|m|}(\eta) \tag{7}$$

which yields a five-term recursion relation,

$$\begin{aligned} &c^2[(l-|m|)(l-|m|-1)/(2l-3)(2l-1)]\,d_{l-2}' - p[(l-|m|)/(2l-1)]\,d_{l-1}' \\ &\quad + \{[l(l+1)-A] + c^2[2l(l+1)-2m^2-1]/(2l-1)(2l+3)\}\,d_l' \\ &\quad - p[(l+|m|+1)/(2l+3)]\,d_{l+1}' \\ &\quad + c^2[(l+|m|+2)(l+|m|+1)/(2l+5)(2l+3)]\,d_{l+2}' = 0. \end{aligned} \tag{8}$$

Given the eigenvalue A, the coefficients d_l' can be found using the inverse iteration technique described by Wilkinson [10]. The coefficients d_l are normalized so that

$$\int_{-1}^{+1} S^2(\eta)\,d\eta = 1. \tag{9}$$

The form (7) has been used by Helfrich [11] to represent the angular parts of the bound state wavefunctions.

2. *Solution of Radial Equation*

We require the solution of Eq. (3) which is regular at $\xi = 1$; it has the asymptotic form

$$X^{\text{reg}}(\xi) = (B/r)\sin[kr + (q/2c)\ln kr + \delta], \tag{10}$$

where r is the distance of the electron from the geometric center, B is a normalization constant and δ is the phase shift; $k = 2c/R$ $(k^2 = \epsilon)$.

To obtain this solution we write

$$X(\xi) = [(\xi-1)/(\xi+1)]^{|m|/2} F(\xi) \tag{11}$$

and $F(\xi)$ satisfies the differential equation

$$(\xi^2-1)\,F''(\xi) + 2(|m|+\xi)\,F'(\xi) + [c^2\xi^2 + q\xi - A]\,F(\xi) = 0. \tag{12}$$

The solution $F^{\text{reg}}(\xi)$ which is regular at $\xi = 1$ is generated as a series in (positive) powers of $(\xi - 1)$ (a four term recursion formula is obtained for the coefficients). This solution is continued numerically by integration of (12) with a variable-step Adams–Moulton–Bashforth predictor–corrector method, until a value of ξ suitable for matching to asymptotic solutions is reached.

The asymptotic solutions to (12) can be written

$$F^{\pm}(\xi) = (\xi + 1)^{-1} \exp \pm i\{c\xi + (q/2c) \ln(\xi + 1)\}\, u^{\pm}(\xi) \tag{13}$$

and if we write

$$u^{\pm}(\xi) = \sum_{n} b_n{}^{\pm}[2/c(\xi + 1)]^n \tag{14}$$

the coefficients $b_n{}^{\pm}$ satisfy a three-term recursion relation,

$$\begin{aligned} &c\{n(n + |m|) - (q/4c^2) \mp i(q/2c)(2n + |m|)\}\, b^{\pm}_{n-1} \\ &\quad - \{n(n + 1) - (q^2/4c^2) + q + c^2 - A \\ &\quad \mp i[(q/2c)(2n + 1) - 2c(2n + |m| + 1)]\}\, b_n{}^{\pm} \pm 4i(n + 1)\, b^{\pm}_{n+1} = 0 \end{aligned} \tag{15}$$

with $b^{\pm}_{-1} = 0$, $b_0{}^{\pm} = 1$. Evidently $u^{-}(\xi) = [u^{+}(\xi)]^{*}$. Equation (14) is an asymptotic expansion; for sufficiently large ξ it yields sufficiently accurate solutions $F^{\pm}(\xi)$. To determine the phase shift δ we write

$$\begin{aligned} F^{\text{reg}}(\xi) &= D[e^{i\alpha}F^{+}(\xi) + e^{-i\alpha}F^{-}(\xi)], \\ F^{\text{reg}\prime}(\xi) &= D[e^{i\alpha}F^{+\prime}(\xi) + e^{-i\alpha}F^{-\prime}(\xi)], \end{aligned} \tag{16}$$

and determine α. From Eqs. (13) and (16) it follows that

$$X^{\text{reg}}(\xi) \sim [\mathscr{C}/(\xi + 1)] \sin[c\xi + (q/2c) \ln c(\xi + 1) + \delta], \tag{17}$$

where

$$\delta = \alpha - (q/2c) \ln c + \pi/2 \tag{18}$$

(note that $c = \frac{1}{2}kR$, $(q/2c) = (Z_A + Z_B)/k$). In the united atom limit, δ tends to the appropriate Coulomb phase shift [9],

$$\delta \xrightarrow[R\to 0]{} \sigma_L - (L\pi/2) + \gamma \ln 2, \tag{19a}$$

where

$$\sigma_L = \operatorname{Arg} \Gamma(L + 1 - i\gamma) \tag{19b}$$

and

$$\gamma = (Z_A + Z_B)/\epsilon^{1/2} = (q/2c). \tag{19c}$$

The phase $\varDelta$ reported by Ponomarev and Somov is related to our phase δ (mod 2π) by

$$\varDelta = \delta + (L\pi/2) - \gamma \ln 2.$$

The phase shifts reported by Levy and Thorson [5b] for $H_2{}^+$ are incorrect; correct values are obtained by subtracting $c = \frac{1}{2}kR$ from their quoted values (cf. also Ref. [12]).

The wavefunctions are normalized to include the density of continuum states, and this requires

$$\mathscr{C} = 2/(2\pi cR)^{1/2} = 2/R(\pi k)^{1/2}. \tag{20}$$

3. *Remarks*

Our method of solution differs in some ways from that used by Ponomarev and Somov [4]: (a) We expand the angular eigenvector $S(\eta)$ in associated Legendre functions (7), while they employ a power series in $(1 + \eta)$. The form (7) is more directly useful in impact ionization calculations, since it yields directly the required asymptotic unitary decomposition into spherical harmonics (Ref. [5a]). (b) We use the extended asymptotic expansions (13), (14) to represent the matching solutions via (16), and this leads to a significant saving in computer time since numerical integration need not be carried as far to obtain a phase shift of given accuracy. Ponomarev and Somov state that for a precision of 1×10^{-7} they require matching at ξ^*_{PS} such that $c\xi^*_{\mathrm{PS}} = 50 \mid A - c^2 - \gamma^2 \mid$; we find that in our case ξ^*_{RT} such that $c\xi^*_{\mathrm{RT}} = 3\gamma$ is sufficient to give phase shifts precise to better than 1×10^{-6} in every case. This appears to be a significant saving in computational effort.

Using an Amdahl 470V/6 digital CPU computation of a single continuum partial wave state, for 12 values of R (1 to 12 a.u.) and 5 values of energy ϵ, 60 solutions in all, requires 9.5 sec CPU time.

Greenland [3] proposes a solution for the continuum states which is not correct. In particular: (a) He attempts to determine the separation constant A by requiring that asymptotically solutions $S(\eta)$ shall have angular momentum eigenstate characteristics. Assuming the constraints he imposes, it can be shown that the states $S(\eta)$ are parity eigenstates regardless of the charge asymmetry, obviously a false conclusion. (b) He expands the radial solutions in Coulomb waves and attempts to determine the phase shifts from conditions related to *normalization* of the expansion coefficients. In view of similarities between the radial equation (3) and the radial equation for Coulomb wavefunctions, it at first seems that an expansion based on the latter would provide a useful representation of solutions to (3). However, we show in the Appendix that this is not the case. Greenland and Greiner [12] give a later discussion in terms of Coulomb wavefunctions, in which the errors in Greenland's paper are noted.

The method of Cayford *et al.* [2], which is based on finite difference methods, can be used to calculate continuum states using appropriate boundary conditions at a (previously chosen) fixed point ($\xi = \xi_0$); however, the values of continuum energy then obtained cannot be specified in advance, and this is a significant disadvantage in computational tasks which require calculations at a given constant value of ϵ. Our method and that of Ref. [4] provide direct results for arbitrarily specified ϵ.

C. Results

We label the continuum states with energy ϵ (in Rydbergs), united-atom-limit angular momentum quantum number L, and azimuthal quantum number m.

Table I gives representative values for separation constants A and phase shifts δ in HeH^{2+}; data shown are for $\epsilon = 1.0$ Ry, and states $s\sigma$ ($L = m = 0$), $p\sigma$ ($L = 1, m = 0$), and $p\pi$ ($L = 1, m = 1$) for $0 \leqslant R \leqslant 12$ a.u. In united atom limit the phase shifts all agree (mod 2π) with the appropriate Coulomb phase shifts (19).

Figures 1 and 2 show separation constants A and phase shifts δ, resp., for the model

TABLE I

Separation Constants and Phase Shifts for HeH[a]

	$s\sigma$ wave		$p\sigma$ wave		$p\pi$ wave	
R	A	δ	A	δ	A	δ
0.0	0.000000	0.32661	2.000000	1.42903	2.000000	1.42903
0.5	−0.019726	0.21542	2.061212	1.48671	2.000083	1.39992
1.0	−0.067583	0.08905	2.231426	1.54631	2.001287	1.33885
1.5	−0.119657	−0.02076	2.480920	1.52845	2.006210	1.26945
2.0	−0.154305	−0.22892	2.780038	1.47423	2.018430	1.19966
2.5	−0.157431	−0.20910	3.106771	1.40952	2.041735	1.13187
3.0	−0.121627	−0.29334	3.448244	1.3457	2.079508	1.06667
3.5	−0.044246	−0.37280	3.800033	1.27934	2.134352	1.00411
4.0	0.074055	−0.44815	4.164259	1.21740	2.207954	0.94408
4.5	0.230295	−0.51974	4.547059	1.15752	2.301088	0.88642
5.0	0.419874	−0.58781	4.956207	1.09926	2.413727	0.83100
5.5	0.637180	−0.65248	5.399372	1.04218	2.545180	0.77770
6.0	0.876168	−0.71384	5.882991	0.98597	2.694259	0.72643
6.5	1.130917	−0.77200	6.411565	0.93045	2.859430	0.67709
7.0	1.396101	−0.82707	6.987263	0.87558	3.038956	0.62962
7.5	1.667318	−0.87921	7.609767	0.82142	3.231025	0.58394
8.0	1.941226	−0.92858	8.276389	0.76813	3.433846	0.53999
8.5	2.215513	−0.97539	8.982417	0.71591	3.645729	0.49768
9.0	2.488734	−1.01984	9.721666	0.66497	3.865132	0.45694
9.5	2.760112	−1.06213	10.487144	0.61552	4.090694	0.41771
10.0	3.029326	−1.10245	11.271748	0.56773	4.321242	0.37990
10.5	3.296346	−1.14098	12.068871	0.52174	4.555787	0.34345
11.0	3.561303	−1.17788	12.872869	0.47758	4.793513	0.30828
11.5	3.824407	−1.21327	13.679304	0.43529	5.033756	0.27432
12.0	4.085888	−1.24730	14.484988	0.39480	5.275984	0.24149

[a] $\epsilon = 1.0$ Ry and δ is in units of π.

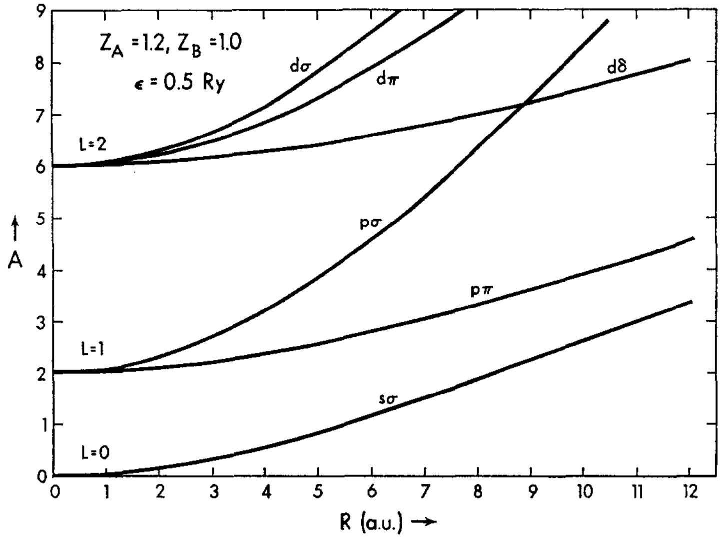

FIG. 1. Separation constants, A, vs R, for the model system $Z_A = 1.2$, $Z_B = 1.0$, energy $\epsilon = 0.5$ Ry, for the first six partial waves.

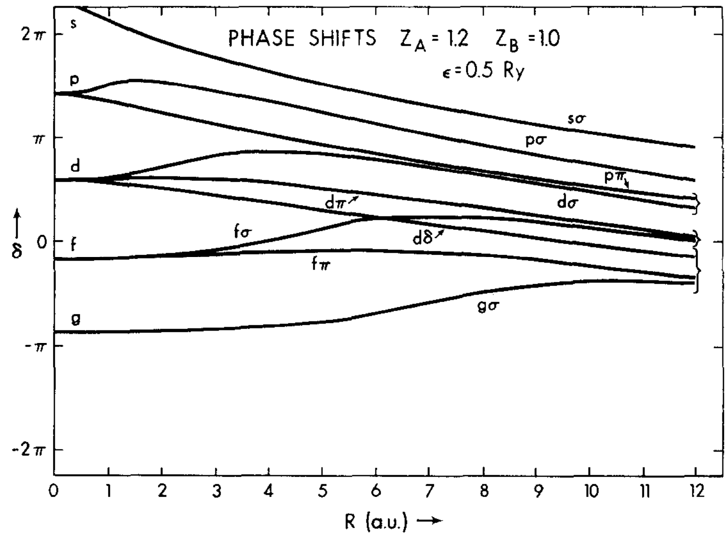

FIG. 2. Phase shifts, δ, vs R, for the model system $Z_A = 1.2$, $Z_B = 1.0$, energy $\epsilon = 0.5$ Ry. Note the ordering in groups at large R values (see text).

system with $(Z_A/Z_B) = 1.2$, at $\epsilon = 0.5$ Ry. The results may be applied directly to a real bare-nucleus system with (Z_A', Z_B') integers, e.g., (6, 5) and (12, 10): simply scale all distances as $(Z_B')^{-1}$, all energies as $(Z_B')^2$.

Figure 3 depicts phase shifts for HeH^{2+} again, at $\epsilon = 1.0$, for the same states as in

Fig. 2. It is interesting to note the systematic interleaving and ordering of phase shifts in the large R region (when plotted mod(2π) as shown) which appear in both these figures. They appear to be grouped according to the values of ($L + |m|$), with phase shifts decreasing as that index increases; within any group of given ($L + |m|$), they are ordered by the value of L, with phase shifts decreasing as L increases, and members of a group never cross each other. This behavior seems to be quite general for all charge ratios and energies.

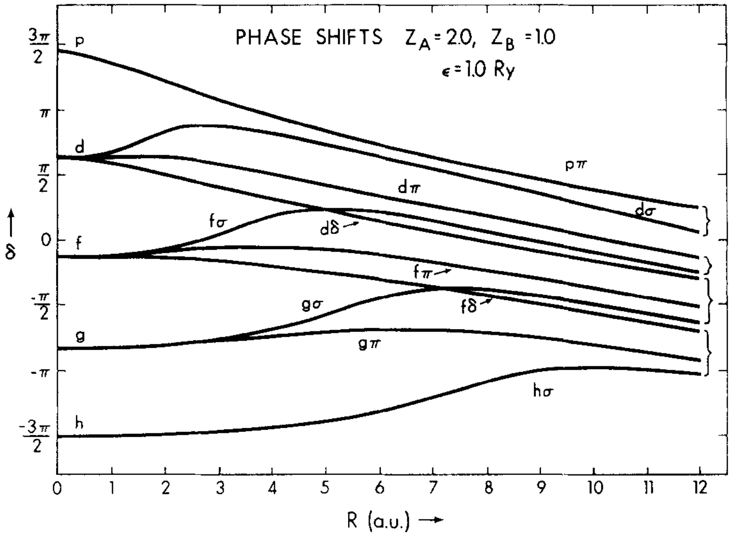

FIG. 3. Phase shifts, δ, vs R, for HeH^{2+}, energy $\epsilon = 1.0$ Ry.

Copies of the FORTRAN IV programs used, and more detailed phase shift and separation constant data, are available upon request from this laboratory.

APPENDIX: EXPANSION OF RADIAL SOLUTION IN COULOMB FUNCTIONS

If we write the solution $X(\xi)$ to Eq. (3) in the form

$$X(\xi) = [(\xi - 1)/(\xi + 1)]^{|m|/2}\{(\xi - 1)^{-1} y(\xi)\} \tag{A.1}$$

and change the independent variable to $x = c(\xi - 1)$, we find for $y(x)$ the equation

$$x(x + 2c)\{y'' + (1 + q/cx)y\} + 2c(|m| - 1)(y' - y/x) + \{c^2 - q - A\}y = 0. \tag{A.2}$$

Now, the spherical Coulomb wavefunctions satisfy the equation [9]

$$F_L'' + [1 + 2\gamma/x - L(L + 1)/x^2]\, F_L = 0, \tag{A.3}$$

where $2\gamma = (q/c) = 2(Z_A + Z_B)/\epsilon^{1/2}$. Suppose then that we write

$$y(x) = \sum_{L=0}^{\infty} \alpha_L F_L(x). \tag{A.4}$$

Upon substitution in Eq. (A.2), after some manipulations using the recursion relations obeyed by the Coulomb functions, we obtain a recursion relation for the coefficients α_L,

$$\begin{aligned} &\{2c(L - |m|)[\gamma^2 + L^2]^{1/2}/(2L - 1)\}\, \alpha_{L-1} + \{L(L+1) + c^2 - A\}\, \alpha_L \\ &\quad + \{2c(L + |m| + 1)[\gamma^2 + (L+1)^2]^{1/2}/(2L+3)\}\, \alpha_{L+1} = 0 \end{aligned} \tag{A.5}$$

with initial conditions $\alpha_{-1} = 0$, $\alpha_0 = 1$. For very large L, the coefficients satisfy either

$$\alpha_{L+1} \simeq -(L/c)\, \alpha_L \tag{A.6a}$$

or

$$\alpha_L \simeq -(c/L)\, \alpha_{L-1}. \tag{A.6b}$$

In order to satisfy the initial conditions, we must choose the solution which behaves like (A.6a), i.e., the coefficients increase factorially, like those in a typical asymptotic expansion. Now, for small values of x, where the Coulomb functions can be represented by the power series form of the confluent hypergeometric function, the growth of these coefficients is offset by the factorially decreasing size of $F_L(x)$ and this solution has the general properties of a power series solution for $y(x)$.

For large x, where $F_L(x)$ has the form

$$F_L(x) \sim \sin[x + \gamma \ln 2x - L\pi/2 + \sigma_L],$$

the series is useless for representing $y(x)$ and indeed appears to diverge.

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