

Asymptotic Expansions of Mathieu Functions in Wave Mechanics

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Solutions of the radial Schrödinger equation containing a polarisation potential r^{-4} are expanded in a form appropriate for large values of r . These expansions of the Mathieu Functions are used in association with the numerical solution of the Schrödinger equation, to impose the asymptotic boundary condition in the case of bound states, and to extract phase shifts in the case of scattering states.

1. INTRODUCTION

The radial Schrödinger equation containing a potential $V(r)$ proportional to $\pm r^{-4}$ has been studied quite extensively. In the case of a repulsive potential ($+r^{-4}$) the physical interest arises because the nucleon-nucleon interaction is thought to have a similar, highly singular form [1-3]. An attractive potential ($-r^{-4}$) is the form of the interaction between an ion and a neutral atom or molecule at moderate to large distances. Studies of this ion-neutral interaction have been concerned with predicting the contribution to the phase shifts caused by the polarisation potential $-r^{-4}$ [4-8].

In view of the physical interest it is appropriate to solve the repulsive problem throughout the whole range of $r(0 \text{ to } \infty)$, whereas in the attractive (ion-neutral) case the physical potential deviates from the polarisation form ($-r^{-4}$) at small values of r . Thus in this latter case it is only appropriate to express the radial wavefunction as a Mathieu function at moderate to large values of r , which is the domain of validity of the expansions presented in this paper. Mathematically these asymptotic expansions are applicable to either the attractive or repulsive potentials for large values of the argument.

2. THE COMPUTATIONAL PROBLEM

The problem of concern in this paper is the solution of the radial Schrödinger equation containing a known potential $V(r)$, which becomes a polarization poten-

tial $-z^2\alpha/(2r^4)$ within the required precision for $r > r_{\text{pol}}$; the value r_{pol} increases with the required precision of the potential. For the ion-neutral interaction α is the static electric dipole polarizability of the neutral atom or molecule, and z is the charge on the ion in atomic units [5, 6]. For $r < r_{\text{pol}}$ the potential $V(r)$ will not generally have a simple analytical form, so that the Schrödinger equation must be solved numerically [9].

A problem in numerical practice is the choice of the upper limit on the range of integration (r_{max}), since in principle this range extends up to $r = \infty$. One might choose this upper limit to be sufficiently large for $V(r_{\text{max}})$ to be equal to its constant, asymptotic value within the precision of the calculation. If r_{max} is chosen in this way, then it may be very large (hundreds of atomic units), so that a large amount of computer time is incurred, and accumulated rounding errors may limit the precision of the numerical solution [10].

In cases such as the ion-neutral interaction in which $V(r)$ becomes a polarization potential as r becomes large (at $r = r_{\text{pol}}$ within the required precision), r_{max} can be chosen to be any value greater than r_{pol} . The Schrödinger equation is integrated numerically between $r = 0$ and $r = r_{\text{max}}$, and the numerical solution is matched to the general semi-analytical solution of the radial Schrödinger equation containing the polarization potential, which is a Mathieu function [11, 12, 13, Chap. 20].

Thus one needs a semianalytical form for these Mathieu functions suitable for evaluation at moderate to large values of r . The purpose of this paper is to present the expansions of these Mathieu functions which we have derived, and to show how they may be matched to the numerical solution obtained in the range $0 < r < r_{\text{max}}$. This matching procedure imposes the appropriate upper boundary condition on the wave function in the case of bound states, and determines phase shifts in the case of scattering states.

The expansions of the Mathieu functions used in previous work [1-12] are not particularly suitable for the application considered here, because they involve series in both integral and inverse powers of r (r^n : $-\infty \leq n \leq +\infty$), and the determination of a characteristic exponent. This is an eigenvalue problem, so that it necessarily leads to iterative numerical procedures. The expansions presented below contain the asymptotic form of the wave function as a factor, and are based upon series in r^{-1} , so that the characteristic exponent is not needed. These asymptotic expansions of the Mathieu functions are related to the large-argument expansions of the spherical Bessel functions [13, p. 437, Sect. 10.1.8 and 10.1.9] in the case of zero polarizability ($\alpha = 0$). They are evaluated by noniterative summation of a sufficient number of terms of the series, until the next term to be added is smaller than the tolerable error in the sum.

3. THE FORM OF THE SOLUTION

The radial Schrödinger equation is usually simplified by removing a factor of r^{-1} from the wave function $\psi(r)$ [14, p. 266]; $\psi(r) = y(r)/r$. This removes the first derivative term from the equation. The equation for $y(r)$ has the form:

$$d^2y/dr^2 + [2\mu(E - V_\infty) + \mu\alpha/r^4 - l(l+1)/r^2] y = 0. \quad (1)$$

This form implies the use of atomic units [15, p. xv]. μ is the reduced mass of the two interacting particles, V_∞ is the asymptotic limit of the potential, and l is the angular momentum quantum number.

For scattering states ($E > V_\infty$) it is convenient to define a real parameter

$$k = [2\mu(E - V_\infty)]^{1/2}. \quad (2a)$$

For bound states ($E < V_\infty$) this parameter is defined by

$$k = [2\mu(V_\infty - E)]^{1/2}, \quad (2b)$$

so that k is real and positive in both cases. For both bound and scattering states simplification then proceeds by transformation to an independent variable $z = kr$, and by the introduction of a real parameter $\theta = \mu\alpha k^2$. Thus Eq. (1) is reduced to one containing only two parameters (θ and l):

$$d^2f/dz^2 + [\theta/z^4 - l(l+1)/z^2 \pm 1] f = 0, \quad (3\pm)$$

where $f(z) = y(r)$. The upper (+) sign is for the case of scattering states, and the lower (−) sign for that of bound states.

The asymptotic form of $f(z)$ as $z \rightarrow \infty$ is obtained by solving the equation:

$$d^2f_\infty/dz^2 \pm f_\infty = 0. \quad (4)$$

For scattering states this produces $f_\infty \simeq \exp(\pm iz)$, and for bound states $f_\infty \simeq \exp(\pm z)$.

We note in passing that the form of $f(z)$ for small values of z is obtained by solving (3) retaining only the term θ/z^4 . The form is the same for bound and scattering states, $f \simeq \exp(\pm i\theta^{1/2}/z)$, which exhibits the increasingly oscillatory behavior of the Mathieu function as $z \rightarrow 0$ [4]. Since the real potential $V(r)$ is not of the polarization form $-r^{-4}$ at small values of r , it is not appropriate to introduce this factor into $f(z)$.

The physically correct asymptotic form of $f(z)$ for bound states is $\exp(-z)$; eliminating $\exp(+z)$ in effect fixes one of the arbitrary constants in the general solution of Eq. (3−). For scattering states it is sufficient to consider only one of

the forms, $\exp(iz)$ or $\exp(-iz)$, in order to obtain the general solution, because the real and imaginary parts of the other factor of $f(z)$ ($g(x)$ below) are linearly independent [11, p. 222]. Arbitrarily we choose $\exp(-iz)$ as the asymptotic factor of $f(z)$.

4. SERIES EXPANSION OF $f(z)$

The series expansions for bound states and for scattering states, may be developed together by transforming to the independent variable $x = iz$ in the case of scattering states, and by simply writing $x = z$ for bound states. The transformation $x = iz$ is actually necessary in order to develop the series for $f(z)$ [11, p. 221, Sect. 11.20]. Thus $f(z)$ is written as a product:

$$f(z) = \exp(-x) g(x). \quad (5)$$

The equation determining $g(x)$ is obtained by substituting (5) into (3 \pm):

$$d^2g/dx^2 - 2dg/dx - [l(l+1)/x^2 \pm \theta/x^4] g = 0, \quad (6\pm)$$

where as in (3 \pm) the upper (+) sign refers to scattering states ($x = iz$) and the lower (-) sign refers to bound states ($x = z$).

The factor $g(x)$ is expanded as a series in inverse powers of x :

$$g(x) = \sum_{j=0}^{\infty} C_j/x^j, \quad (7)$$

where we have anticipated that the indicial index is zero. Substitution of (7) into (6 \pm) followed by the usual series solution procedure of setting the coefficient of each power of x to zero [16, Sect. 2.11], yields the equations:

$$\begin{aligned} C_0 &= \text{an arbitrary constant} \\ 2 C_1 &= l(l+1) C_0 \\ 4 C_2 &= [l(l+1) - 2] C_1 \\ 2j C_j &= [l(l+1) - j(j-1)] C_{j-1} \pm \theta C_{j-3} \\ & \quad j = 3, 4, 5, \dots \end{aligned} \quad (8\pm)$$

The upper sign (+) refers to scattering states, and the lower (-) sign to bound states.

It is apparent from (8 \pm) that the sequence of coefficients C_j diverges as j becomes large, so that the higher order terms of (7) involve division of one large number (C_j) by another large number (x^j). In our experience [17] this leads to the numerical

problem that C_j and x^j go outside the range of the floating point arithmetic of the computer being used, even though the quotient C_j/x^j remains within range.

This numerical problem is circumvented by re-expressing $g(x)$ as a simple sum of terms, so that the coefficients C_j are never explicitly calculated. For both bound and scattering states a term T_j is defined by:

$$T_j = C_j/z^j, \tag{9}$$

where we have transformed back to the real variable z in the case of scattering states. For bound states $g(z = x)$ is given by:

$$g(z) = \sum_{j=0}^{\infty} T_j. \tag{10}$$

For scattering states the real and imaginary parts of the complex conjugate of $g(x)$ are denoted by $P(z)$ and $Q(z)$;

$$g(x = iz) = P(z) - iQ(z), \tag{11}$$

so that P and Q are sums of the real terms T_j :

$$P = \sum_{j=0}^{\infty} (-1)^j T_{2j}; \quad Q = \sum_{j=0}^{\infty} (-1)^j T_{2j+1}. \tag{12}$$

The recurrence relations between the T_j for both bound and scattering states are obtained by substituting (9) (i.e., $C_j = T_j z^j$) into (8 ±):

$$\begin{aligned} T_0 = C_0 &= \text{an arbitrary constant} \\ 2zT_1 &= l(l+1) T_0 \\ 4zT_2 &= [l(l+1) - 2] T_1 \\ \bullet \quad 2jzT_j &= [l(l+1) - j(j-1)] T_{j-1} \pm \theta T_{j-3}/z^2 \end{aligned} \tag{13}$$

where as in (3 ±) and (6 ±), the upper (+) sign refers to scattering states, and the lower (−) sign to bound states. In practice the infinite summations in (10) and (12) are terminated when $g(x)$ has become constant to the required precision [17]. This is equivalent to the requirement that the next term to be added is smaller than the tolerable error in the sum. This convergence criterion is sufficient to guarantee the required accuracy of the evaluated function, even though the asymptotic series ultimately diverges [24, Chap. 21]. Since this convergence requirement can only be met for sufficiently large values of $z = kr$, nonconvergence to the required accuracy was monitored by terminating the summation after a arbitrarily preset number of terms (in practice 30 terms).

5. BOUND STATE MATCHING PROCEDURE

Typical methods of numerical integration of the radial Schrödinger equation [9, 18–20] involve a finite-difference relation between three adjacent values of $y(r)$; $y(r_{\max} - h)$, $y(r_{\max})$, and $y(r_{\max} + h)$, where h is the step length of the finite-difference grid of points.

The matching procedure is very simple. C_0 is given an arbitrary value to fix the normalization of the wavefunction; in practice a small number is appropriate since the relative magnitude of the wave function is small at the large distance r_{\max} . The two values $y(r_{\max})$ and $y(r_{\max} + h)$ are evaluated by Eqs. (5), (10), and (13). These two values of y are then used in the finite-difference relation to generate $y(r_{\max} - h)$ to begin the process of inward integration [9]. In this way the upper boundary condition on $y(r)$ is automatically imposed on the generated numerical solution.

6. EXTRACTION OF SCATTERING STATE PHASE SHIFTS

The real and imaginary parts of the complex conjugate of $f(z)$ are $P \cos z - Q \sin z$ and $P \sin z + Q \cos z$. Thus the general solution of (3+) is:

$$f_g(z) = \gamma[P \cos z - Q \sin z] + \beta[P \sin z + Q \cos z] \quad (14)$$

where γ and β are arbitrary constants.

For scattering states, numerical integration of the radial Schrödinger equation can be started at $r = 0$ and carried outwards to $r = r_{\max}$ [18, 21]. $P(z)$ and $Q(z)$ are calculated with $C_0 = 1$ (arbitrary normalization) for $z = k r_{\max}$ and $z = k(r_{\max} - h)$. The constants γ and β are then determined by equating $f_g(z)$ (Eq. (14)) to the numerical solution $f(z)$ at $r = r_{\max}$ and $r = r_{\max} - h$.

Since $P \rightarrow 1$ and $Q \rightarrow 0$ as $r \rightarrow \infty$, the asymptotic form of $f_g(z)$ is

$$f_g(z) \rightarrow \gamma \cos z + \beta \sin z. \quad (15)$$

In partial wave analysis [22, p. 29] the radial wavefunction has the asymptotic form

$$y \simeq \sin(z - (l\pi/2) + \delta_l) \quad (16)$$

where δ_l is the scattering phase shift. Equations (15) and (16) yield the relation determining δ_l :

$$\tan(\delta_l - (l\pi/2)) = \gamma/\beta. \quad (17)$$

This method of determining phase shifts has been applied to the scattering of electrons, protons, and positrons, from hydrogen atoms [17, 23]. We have also

compared phase shifts obtained by the method presented in this paper with the "polarization phase shifts ρ_l " as defined by Holzwarth [4]. For large values of the angular momentum l , when ρ_l dominates the total scattering phase shift, there is excellent agreement between the two methods.

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