RADIAL: a FORTRAN subroutine package for the solution of the radial Schrödinger and Dirac wave equations

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Abstract

The FORTRAN 77 subroutine package RADIAL for the numerical solution of the Schrödinger and Dirac wave equations for central fields is described. The considered fields are such that the function $\mathcal{V}(r) \equiv rV(r)$ is finite for all r and tends to constant values for $r \to 0$ and $r \to \infty$. This includes finite-range fields as well as combinations of Coulomb and short-range fields. The potential energy function $\mathcal{V}(r)$ used in the calculation is the natural cubic spline that interpolates a table of values provided by the user. The radial wave equations are solved by using piecewise exact power series expansions of the radial functions, which are summed up to the prescribed accuracy so that truncation errors can be completely avoided. Normalized radial wave functions, eigenvalues for bound states and phase shifts for free states are evaluated.

Keywords: Schrödinger equation. Dirac equation. Central fields. Bound states, eigenvalues. Free states, phase shifts. Coulomb functions. Bessel functions.

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1 Introduction

The calculation of central-field radial wave functions is a basic tool in atomic and nuclear physics. In spite of its practical importance, computer programs, capable of solving the radial wave equations for an arbitrary field $V(r)$ given in numerical form, are not generally available. In this report we describe an algorithm, and a `FORTRAN 77` subroutine package called `RADIAL`, for the numerical solution of the radial Schrödinger and Dirac equations for a wide class of central fields. The potentials considered are such that the function $\mathcal{V}(r) \equiv rV(r)$ is finite for all r and reaches constant values when $r \to 0$ and $r \to \infty$. This includes finite-range fields as well as Coulomb fields and any combination of Coulomb and short-range fields (the so-called modified Coulomb fields).

The present report is intended to serve as a manual of the subroutine package. You can obtain it by running the file `RADIAL.TEX`, which should accompany the `FORTRAN` source files, through LaTeX and printing the output file. For the sake of completeness, we offer a detailed description of the solution algorithm, including the complete collection of formulae and numerical recipes used in the program. This information may be helpful to correct possible bugs in the computer code (which do have a tendency to come into action when programs leave the author's hand).

The numerical procedures adopted to solve the radial differential equations have been described by Salvat and Mayol (1991). The function $\mathcal{V}(r)$ used in the calculations is the natural cubic spline (see appendix A) that interpolates the values of a table provided by the user. Interpolation errors introduced by the spline approximation can be made as small as required by simply specifying the values of the potential function in a sufficiently dense grid of points. The responsibility for ensuring that the effect of these interpolation errors on the calculation results is negligible rests with the user. In this respect, it may be helpful to plot the input potential table together with the spline interpolation and check that the spline does not wiggle between the input data points. The radial wave equations for the cubic spline field are solved by using the *exact* power-series expansions of the radial functions, which are summed up to a prescribed accuracy. This procedure allows a complete control of truncation errors. The calculation results are thus only affected by unavoidable round-off errors. In practice, the algorithm permits different levels of accuracy; the price to be paid for a more accurate result is merely a longer calculation time. With double-precision arithmetic, results accurate to up to 13 or 14 decimal figures can be obtained.

The `FORTRAN 77` subroutine package `RADIAL` presented here has been tailored to be as easy to use as possible. Although it is largely based on the `RADWEQ` package of Salvat and Mayol (1991), it is considerably more versatile and general. The main added features are:

1. Modified Coulomb fields (i.e. fields such that $\lim_{r\to\infty} \mathcal{V}(r) = Ze^2$, a constant) are considered.

2. Free-state wave functions are properly normalized.

3. The radial functions are calculated for a specified (arbitrary) grid of points, which may be different from the grid where the potential function is tabulated.

4. The package includes a group of high-accuracy subroutines that compute Schrödinger- and Dirac-Coulomb functions, and spherical Bessel functions, which are required to normalize free-state radial functions.

The input/output of both packages is identical, so that programs using the old `RADWEQ` package can be directly linked to `RADIAL`; however, the calculation with `RADIAL` may be slightly slower in some cases.

2 Radial wave equations

2.1 Schrödinger equation

In non-relativistic quantum mechanics, the stationary states of a particle in a central potential $V(r)$ are described by the time-independent Schrödinger equation

$$\mathcal{H}_{\mathrm{S}}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{1}$$

with the Hamiltonian

$$\mathcal{H}_{\mathrm{S}} = -\frac{\hbar^2}{2M}\nabla^2 + V(r) = -\frac{\hbar^2}{2M}\left(\frac{1}{r}\frac{\partial^2}{\partial\, r^2}r - \frac{1}{r^2}L^2\right) + V(r), \tag{2}$$

where M is the mass of the particle and $\hbar$ is the reduced Planck constant. Since the orbital angular momentum operator (in units of $\hbar$) $\mathbf{L} = (1/\hbar)\mathbf{r}\times\mathbf{p}$ commutes with $\mathcal{H}_{\mathrm{S}}$, we can construct simultaneous eigenfunctions of $\mathcal{H}_{\mathrm{S}}$, L^2 and L_z. These solutions of the Schrödinger equation are of the form

$$\psi(\mathbf{r}) = \frac{1}{r}P(r)Y_{\ell,m}(\hat{\mathbf{r}}), \tag{3}$$

where the spherical harmonics $Y_{\ell,m}(\hat{\mathbf{r}})$ are eigenfunctions of L^2 and L_z (with eigenvalues $\ell(\ell+1)$ and m, respectively) and the reduced radial function $P(r)$ satisfies the radial equation

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2P}{\mathrm{d}r^2} + \left[\frac{\hbar^2}{2M}\frac{\ell(\ell+1)}{r^2} + V(r)\right]P = EP. \tag{4}$$

Since $rV(r)$ is finite everywhere, we can require that the wave function $\psi(\mathbf{r})$ also be finite in all space. This implies that the radial function $P(r)$ behaves as $r^{\ell+1}$ near the origin (see subsection 4.1).

When $V(r)$ takes negative values in a certain region, bound states may exist, where the particle is constrained to move within a limited volume, for a discrete set of negative eigenvalues. Discrete energy levels can be identified by the angular momentum quantum number ℓ and the principal quantum number n. Alternatively, instead of n, the radial

quantum number $n_{\rm r} = n - (\ell + 1)$ can be used to label the negative energy levels. The radial quantum number has a more direct geometrical significance: it gives the number of nodes of the radial function, i.e. the zeros of $P(r)$ other than those at $r = 0$ and $r = \infty$. It is instructive to consider the radial motion under the effective potential

$$V_{\rm eff}(r) = \frac{\hbar^2}{2M}\frac{\ell(\ell+1)}{r^2} + V(r).$$

From the structure of the differential equation (4), it can be easily shown that the nodes of the radial function are located in the classically allowed region of motion. Evidently, the set of inflexion points ($\mathrm{d}^2P/\mathrm{d}r^2 = 0$) of the radial function consists of the nodes of $P(r)$ and the turning points of the radial motion ($V_{\rm eff} = E$). In the classically forbidden region, $P(r)$ increases, or decreases, monotonously when r increases. As eq. (4) does not depend on the magnetic quantum number m, each energy level $E_{n\ell}$ is at least, $2\ell+1$ times degenerate (the energy levels of a pure Coulomb field are also degenerate with respect to ℓ). For bound states, the radial function is normalized by requiring

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int_0^\infty P^2(r)\,\mathrm{d}r = 1. \tag{5}$$

For free states ($E > 0$, continuum spectrum), the wave function will be normalized to the asymptotic form

$$P(r) \sim \sin\left(kr - \ell\frac{\pi}{2} - \eta\ln 2kr + \delta\right), \tag{6}$$

where

$$k \equiv \frac{p}{\hbar} = \sqrt{2ME}/\hbar \tag{7}$$

is the particle wave number, η is a constant (=0 for finite-range fields) and δ is the phase shift.

2.2 Dirac equation

Stationary states of a relativistic particle with spin 1/2 in the field $V(r)$ are described by the Dirac equation

$$\mathcal{H}_{\rm D}\psi(\mathbf{r}) = (E + Mc^2)\psi(\mathbf{r}) \tag{8}$$

with the Hamiltonian

$$\mathcal{H}_{\rm D} = -\mathrm{i}\,c\hbar\,\vec{\alpha}\cdot\vec{\nabla} + \beta Mc^2 + V(r), \tag{9}$$

where $\vec{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and β are 4×4 matrices. In the spinor representation

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} \mathrm{I}_2 & 0 \\ 0 & -\mathrm{I}_2 \end{pmatrix}. \tag{10}$$

Here, $\vec{\sigma}$ stands for the familiar Pauli spin matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{11}$$

and I_2 is the 2×2 unit matrix. In this representation, $\psi(\mathbf{r})$ is a four-component function. We note that the quantity E in eq. (8) is the energy of the particle *excluding* the rest energy Mc^2; in the non-relativistic limit ($c \to \infty$), the "eigenvalues" E of the Dirac equation (8) tend to the eigenvalues of the Schrödinger equation (1) (see below).

The angular momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where $\mathbf{L}$ is the orbital angular momentum operator and $\mathbf{S} = (1/2)\vec{\sigma}$ the spin operator, commutes with the Dirac Hamiltonian. The operator

$$\mathcal{K} \equiv -\beta\,(\vec{\sigma}\cdot\mathbf{L}+1) = \begin{pmatrix} -\left(J^2 - L^2 + \frac{1}{4}\right)\mathrm{I}_2 & 0 \\ 0 & \left(J^2 - L^2 + \frac{1}{4}\right)\mathrm{I}_2 \end{pmatrix} \tag{12}$$

commutes with $\mathcal{H}_\mathrm{D}$, J^2 and J_z. Therefore, we can construct simultaneous eigenfunctions of $\mathcal{H}_\mathrm{D}$, J^2, J_z and $\mathcal{K}$, with eigenvalues $E + Mc^2$, $j(j+1)$, m and κ, respectively. Such solutions of the Dirac equation can be written as[1]

$$\psi(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} \mathrm{i}P(r)\,\Omega_{\kappa,m}(\hat{\mathbf{r}}) \\ Q(r)\,\Omega_{-\kappa,m}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{13}$$

where $P(r)$ and $Q(r)$ are the upper- and lower-component radial functions and the spherical spinors

$$\begin{aligned} \Omega_{\kappa,m}(\hat{\mathbf{r}}) \equiv \Omega^{\ell}_{j,m}(\hat{\mathbf{r}}) &= \sum_{\mu=\pm 1/2} \langle \ell, 1/2, m-\mu, \mu | j, m\rangle\; Y_{\ell,m-\mu}(\hat{\mathbf{r}})\chi_\mu \\ &= \begin{pmatrix} \langle \ell, 1/2, m-1/2, +1/2 | j, m\rangle\, Y_{\ell,m-1/2}(\hat{\mathbf{r}}) \\ \langle \ell, 1/2, m+1/2, -1/2 | j, m\rangle\, Y_{\ell,m+1/2}(\hat{\mathbf{r}}) \end{pmatrix} \end{aligned} \tag{14}$$

are simultaneous eigenfunctions of L^2, S^2, J^2 and J_z with eigenvalues $\ell(\ell+1)$, $3/4$, $j(j+1)$ and m, respectively. The quantities $\langle \ell, 1/2, m-\mu, \mu | j, m\rangle$ are Clebsch-Gordan coefficients, and the spinors χ_μ are eigenfunctions of S^2 and S_z with eigenvalues $3/4$ and $\mu = \pm 1/2$. The quantum numbers κ, j and ℓ are related by

$$\begin{aligned} &\kappa = (\ell - j)(2j+1) = -(j+1/2)\sigma, \quad \sigma \equiv -\mathrm{sgn}(\kappa) = -|\kappa|/\kappa, \\ &j = |\kappa| - 1/2 = \ell + \sigma/2, \\ &\ell = |\kappa| - (1+\sigma)/2 = j - \sigma/2. \end{aligned} \tag{15}$$

We see that the relativistic wave function (13) is not an eigenfunction of L^2; the index ℓ used in spectroscopic notation is the eigenvalue of the upper-component spinor and serves to indicate the parity of $\psi(\mathbf{r})$. The radial functions $P(r)$ and $Q(r)$ satisfy the coupled equations

$$\begin{aligned} \frac{\mathrm{d}P}{\mathrm{d}r} &= -\frac{\kappa}{r}P - \frac{E - V + 2Mc^2}{c\hbar}Q, \\ \frac{\mathrm{d}Q}{\mathrm{d}r} &= \frac{E-V}{c\hbar}P + \frac{\kappa}{r}Q. \end{aligned} \tag{16}$$

[1] The Dirac wave function (13) conforms to the phase convention adopted by Walker (1971); in the alternative phase convention (see e.g. Rose, 1961) the radial function $Q(r)$ has the opposite sign.

Strictly speaking, these equations determine the wave functions for states with positive total energy ($E + Mc^2 > 0$). The Dirac equation admits negative eigenvalues ($E + Mc^2 < 0$), which correspond to antiparticle states. For instance, in the case of a purely electrostatic field of force, specified by a scalar potential $\phi(r)$, the states of an ordinary electron (negatron) are described by the orbitals (13), whose radial functions are solutions of eqs. (16) with $V(r) = -e\phi(r)$, where e is the absolute value of the electron charge. Negative energy states for such a field represent positron states, they are of the form (see e.g. Rose, 1961, p. 160)

$$\psi(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} Q(r)\,\Omega_{-\kappa,-m}(\hat{\mathbf{r}}) \\ -\mathrm{i}P(r)\,\Omega_{\kappa,-m}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{17}$$

where the radial functions $P(r)$ and $Q(r)$ satisfy eqs. (16) with the potential function $V(r) = e\phi(r)$.

As in the non-relativistic theory, when $V(r)$ takes negative values in a certain region, bound states may exist for a discrete set of negative eigenvalues. Discrete energy levels are now identified by the quantum number κ and either the principal quantum number n or the radial quantum number n_r. Again, n_r gives the number of nodes of $P(r)$, which occur only in the classically allowed region of movement (Rose, 1961). Each bound level is, at least, $2j + 1$ times degenerate (the eigenstates of a pure Coulomb field with the same ℓ and $j = \ell \pm 1/2$ have the same energy). Adequate normalization for bound states is

$$\int \psi^\dagger(\mathbf{r})\psi(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int_0^\infty \left[P^2(r) + Q^2(r)\right] \mathrm{d}r = 1. \tag{18}$$

Dirac free states ($E > 0$) will be normalized in such a way that the radial function $P(r)$ asymptotically oscillates with unit amplitude (cf. eq. (6)),

$$P(r) \sim \sin\left(kr - \ell\frac{\pi}{2} - \eta \ln 2kr + \delta\right), \tag{19}$$

where

$$k \equiv \frac{p}{\hbar} = \frac{\sqrt{E(E + 2Mc^2)}}{c\hbar} \tag{20}$$

is the relativistic wave number, η is a constant (=0 for finite range fields) and δ is the phase shift.

It is worth noting that in the limit $E - V \ll 2Mc^2$, the radial eqs. (16) reduce to

$$Q = \frac{c\hbar}{2Mc^2}\left(-\frac{\kappa}{r}P - \frac{\mathrm{d}P}{\mathrm{d}r}\right) \tag{21}$$

and

$$\frac{\mathrm{d}^2P}{\mathrm{d}r^2} = \left[\frac{\kappa(\kappa+1)}{r^2} - \frac{2M}{\hbar^2}(E - V)\right] P. \tag{22}$$

Eq. (21) shows that the lower (small) component $Q(r)$ vanishes in the non-relativistic limit ($c \to \infty$). Using the fact that $\kappa(\kappa + 1) = \ell(\ell + 1)$, eq. (22) is seen to coincide with the Schrödinger equation (4), and therefore, in the non-relativistic limit the upper (large) component $P(r)$ reduces to the Schrödinger radial function.

2.3 Normalization of free-state radial wave functions

As free-state wave functions are not square integrable, they cannot be assigned a finite norm. Instead it is natural to require that their scalar product be proportional to a delta function. In certain applications, it is convenient to use Dirac free-state wave functions normalized on the energy scale, i.e.

$$\int_0^\infty \left[P_{E\kappa}(r)P_{E'\kappa}(r) + Q_{E\kappa}(r)Q_{E'\kappa}(r)\right] \mathrm{d}r = \delta(E - E'). \tag{23}$$

For Schrödinger free states, the energy normalization condition reads

$$\int_0^\infty P_{E\ell}(r)P_{E'\ell}(r)\, \mathrm{d}r = \delta(E - E'), \tag{24}$$

which can be considered as the non-relativistic limit ($c \to \infty$) of eq. (23). Radial functions normalized on the energy scale have the asymptotic form (cf. eqs. (6) and (19))

$$P_{E\kappa}(r) \sim A_E \sin\left(k_E r - \ell\frac{\pi}{2} - \eta_E \ln 2k_E r + \delta_E\right), \tag{25}$$

where A_E, η_E and δ_E are constants and k_E is the wave number given by eq. (20). The asymptotic behaviour of the lower component Dirac function is determined by the first of eqs. (16). Neglecting terms of order $(1/r)$, we get

$$Q_{E\kappa}(r) \sim -A_E\sqrt{\frac{E}{E + 2Mc^2}} \cos\left(k_E r - \ell\frac{\pi}{2} - \eta_E \ln 2k_E r + \delta_E\right). \tag{26}$$

To determine the normalization constant A_E, we consider the radial eqs. (16)

$$P'_{E\kappa} + \frac{\kappa}{r}P_{E\kappa} = -\frac{E - V + 2Mc^2}{c\hbar}Q_{E\kappa}, \tag{27}$$

$$Q'_{E\kappa} - \frac{\kappa}{r}Q_{E\kappa} = \frac{E - V}{c\hbar}P_{E\kappa}, \tag{28}$$

where the primes denote differentiation with respect to r. Multiplying eqs. (27) and (28) from the left by $Q_{E'\kappa}$ and $P_{E'\kappa}$ respectively,

$$Q_{E'\kappa}P'_{E\kappa} + \frac{\kappa}{r}Q_{E'\kappa}P_{E\kappa} = -\frac{E - V + 2Mc^2}{c\hbar}Q_{E'\kappa}Q_{E\kappa},$$

$$P_{E'\kappa}Q'_{E\kappa} - \frac{\kappa}{r}P_{E'\kappa}Q_{E\kappa} = \frac{E - V}{c\hbar}P_{E'\kappa}P_{E\kappa},$$

and subtracting from each of these two equations the analogous ones obtained by interchanging E and E' everywhere, we get

$$Q_{E'\kappa}P'_{E\kappa} - Q_{E\kappa}P'_{E'\kappa} + \frac{\kappa}{r}\left(Q_{E'\kappa}P_{E\kappa} - Q_{E\kappa}P_{E'\kappa}\right) = \frac{E' - E}{c\hbar}Q_{E'\kappa}Q_{E\kappa},$$

$$P_{E'\kappa}Q'_{E\kappa} - P_{E\kappa}Q'_{E'\kappa} - \frac{\kappa}{r}\left(P_{E'\kappa}Q_{E\kappa} - P_{E\kappa}Q_{E'\kappa}\right) = \frac{E - E'}{c\hbar}P_{E'\kappa}P_{E\kappa}.$$

Subtracting the second from the first of these equations we have

$$P_{E\kappa}P_{E'\kappa} + Q_{E\kappa}Q_{E'\kappa} = \frac{c\hbar}{E-E'}\,\frac{\mathrm{d}}{\mathrm{d}r}\left(Q_{E\kappa}P_{E'\kappa} - P_{E\kappa}Q_{E'\kappa}\right).$$

Then, for any value of r,

$$\int_0^r \left(P_{E\kappa}P_{E'\kappa} + Q_{E\kappa}Q_{E'\kappa}\right)\mathrm{d}r = \frac{c\hbar}{E-E'}\,\Big[Q_{E\kappa}(r)P_{E'\kappa}(r) - P_{E\kappa}(r)Q_{E'\kappa}(r)\Big], \qquad (29)$$

since $P_{E\kappa}(0) = Q_{E\kappa}(0) = 0$. Notice that eq. (29) applies to free *and* bound states. When $r \to \infty$, it shows that a bound state is orthogonal to all states with different energies.

For free states and large enough r-values, introducing expressions (25) and (26) into eq. (29) we obtain

$$\begin{aligned}
&\int_0^r \left(P_{E\kappa}P_{E'\kappa} + Q_{E\kappa}Q_{E'\kappa}\right)\mathrm{d}r \\
&\quad= \frac{c\hbar}{E-E'}A_E A_{E'}\left\{\sqrt{\frac{E}{E+2Mc^2}}\cos\phi_E \sin\phi_{E'} - \sin\phi_E\sqrt{\frac{E'}{E'+2Mc^2}}\cos\phi_{E'}\right\} \\
&\quad= \frac{c\hbar}{E-E'}A_E A_{E'}\left\{\sqrt{\frac{E}{E+2Mc^2}}\sin\Big[\left(k_E - k_{E'}\right)r\Big] + R_{E,E'}(r)\right\}, \qquad (30)
\end{aligned}$$

where ϕ_E stands for the argument of the trigonometric functions in expressions (25) and (26). The quantity

$$\begin{aligned}
R_{E,E'}(r) \;\equiv\; &\sqrt{\frac{E}{E+2Mc^2}}\left(\cos\phi_E\sin\phi_{E'} - \sin\Big[\left(k_E - k_{E'}\right)r\Big]\right) \\
&- \sqrt{\frac{E'}{E'+2Mc^2}}\sin\phi_E\cos\phi_{E'} \qquad (31)
\end{aligned}$$

is seen to vanish when $E = E'$. If $E \neq E'$, $R_{E,E'}(r)$ oscillates infinitely rapidly as $r \to \infty$ and contributes nothing. Hence

$$\begin{aligned}
&\int_0^\infty \left(P_{E\kappa}P_{E'\kappa} + Q_{E\kappa}Q_{E'\kappa}\right)\mathrm{d}r \\
&\quad= A_E A_{E'}\, c\hbar\sqrt{\frac{E}{E+2Mc^2}}\,\frac{k_E - k_{E'}}{E-E'}\;\lim_{r\to\infty}\left\{\frac{1}{k_E - k_{E'}}\sin\Big[\left(k_E - k_{E'}\right)r\Big]\right\} \\
&\quad= A_E A_{E'}\,\frac{E}{k_E}\,\frac{k_E - k_{E'}}{E-E'}\,\pi\,\delta\left(k_E - k_{E'}\right) \;=\; A_E A_{E'}\,\frac{E}{k_E}\,\pi\,\delta\left(E - E'\right) \\
&\quad= A_E^2\,\frac{E}{k_E}\,\pi\,\delta\left(E - E'\right). \qquad (32)
\end{aligned}$$

Comparing this result with eq. (23), we see that

$$A_E = \sqrt{\frac{k_E}{\pi E}} \qquad \text{(Dirac)}. \qquad (33)$$

Therefore, the radial function $P_{E\kappa}(r)$ of Dirac free states normalized in the energy scale oscillates asymptotically with amplitude A_E. The normalizing factor for Schrödinger waves can be obtained as the non-relativistic limit of expression (33)

$$A_E = \sqrt{\frac{k_E}{\pi E}} = \sqrt{\frac{2M}{\hbar^2}\frac{1}{\pi k_E}} \qquad \text{(Schrödinger)}. \tag{34}$$

The subroutine package `RADIAL` gives free-state radial functions normalized to unit amplitude, they must be multiplied by the constant factor A_E to get wave functions normalized on the energy scale.

Another normalization for free states, frequently used in scattering theory, is the so-called "wave-number" normalization,

$$\int_0^\infty \left[P_{E\kappa}(r)P_{E'\kappa}(r) + Q_{E\kappa}(r)Q_{E'\kappa}(r)\right] \mathrm{d}r = \delta(k_E - k_{E'}). \tag{35}$$

From the relation

$$\delta(E - E') = \frac{\mathrm{d}k_E}{\mathrm{d}E}\, \delta(k_E - k_{E'}),$$

it follows that the wave-number normalization constant is

$$A_E^{(\mathrm{wn})} = A_E \sqrt{\frac{\mathrm{d}E}{\mathrm{d}k_E}} = \sqrt{\frac{E + 2Mc^2}{\pi\,(E + Mc^2)}} \qquad \text{(Dirac)}, \tag{36}$$

where use has been made of eq. (20). In the non-relativistic limit, we obtain the well-known result

$$A_E^{(\mathrm{wn})} = \sqrt{\frac{2}{\pi}} \qquad \text{(Schrödinger)}. \tag{37}$$

3 Coulomb functions

In the "outer" asymptotic region, where the potential function $\mathcal{V}(r)$ reaches the constant value $Ze^2 \equiv \lim_{r\to\infty} \mathcal{V}(r)$, the free-state wave function can be expressed as a linear combination of the regular and irregular Coulomb functions. These are the positive energy solutions of the radial equations with the Coulomb potential

$$V(r) = \frac{Ze^2}{r}. \tag{38}$$

Normalized wave functions are obtained by matching the "inner" numerical solution with the properly normalized asymptotic solution (see section 6). Evidently, the feasibility of this procedure rests on the availability of fast numerical algorithms for the calculation of Coulomb functions. A variety of procedures to compute Schrödinger-Coulomb functions can be found, e.g. in the papers of Fröberg (1955) and Bardin et al., (1972). A more exhaustive list of references on this topic is given by Barnett (1981). To the best of our knowledge, general methods to calculate Dirac-Coulomb irregular functions appear to be inexistent to date. In this section we describe the algorithms adopted in `RADIAL` for the calculation of Schrödinger- and Dirac-Coulomb functions. The radial Dirac equations for a Coulomb field are reformulated in a way that permits the evaluation of the regular and irregular solutions in terms of the Schrödinger-Coulomb functions.

3.1 Schrödinger-Coulomb functions

The radial Schrödinger equation (4) for the Coulomb field (38) reads

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2U_\ell}{\mathrm{d}r^2}+\left[\frac{\hbar^2}{2M}\frac{\ell(\ell+1)}{r^2}+\frac{Ze^2}{r}\right]U_\ell=E\,U_\ell, \tag{39}$$

which can be recast in a dimensionless form by introducing the variable $x=kr$, where k is the wave number –see eq. (7). We have

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2}+1-\frac{2\eta}{x}-\frac{\lambda(\lambda+1)}{x^2}\right)U_\lambda(\eta,x)=0, \tag{40}$$

with $\lambda=\ell$. The dimensionless quantity

$$\eta=\frac{Ze^2M}{\hbar^2k}=\frac{Ze^2}{\hbar v} \tag{41}$$

is the Sommerfeld parameter. v is the velocity of the particle. In non-relativistic theory, the angular momentum quantum number ℓ can only take positive integer values. For the sake of generality, however, we consider that λ can take any real value larger than -1. It will be shown in subsection 3.4 that Dirac-Coulomb functions are expressable as Coulomb functions with non-integer λ values.

The regular solution $F_\lambda(\eta,x)$ and the irregular solution $G_\lambda(\eta,x)$ of eq. (40) can be defined by their behaviour near the origin

$$F_\lambda(\eta,x)\sim C_\lambda(\eta)x^{\lambda+1},\qquad G_\lambda(\eta,x)\sim x^{-\lambda}/[(2\lambda+1)C_\lambda(\eta)], \tag{42}$$

where

$$C_\lambda(\eta)=2^\lambda\exp(-\eta\pi/2)\frac{|\Gamma(\lambda+1+\mathrm{i}\eta)|}{\Gamma(2\lambda+2)} \tag{43}$$

and Γ stands for the complex gamma function.

From the differential equation (40), it is seen that the Coulomb functions F_λ and G_λ have a turning point at

$$x_{\mathrm{TP}}[\lambda]=\eta+\sqrt{\eta^2+\lambda(\lambda+1)}. \tag{44}$$

For $x<x_{\mathrm{TP}}[\lambda]$, F_λ and G_λ are positive; F_λ increases monotonously and G_λ decreases monotonously with increasing x. For $x>x_{\mathrm{TP}}[\lambda]$, F_λ and G_λ have an oscillatory behaviour. The normalization constant in eqs. (42) is such that the magnitude of the oscillations approaches unity for large x (cf. eq. (6)):

$$F_\lambda(\eta,x)\sim\sin\theta_\lambda,\qquad G_\lambda(\eta,x)\sim\cos\theta_\lambda, \tag{45}$$

with

$$\theta_\lambda=x-\lambda\frac{\pi}{2}-\eta\ln 2x+\Delta_\lambda, \tag{46}$$

where the Coulomb phase shift Δ_λ is given by

$$\Delta_\lambda=\arg\Gamma\left(\lambda+1+\mathrm{i}\eta\right). \tag{47}$$

Although there is a close relationship between Coulomb functions and confluent hypergeometric functions (see e.g. Morse and Feshbach, 1953; Erdélyi et al., 1953), the strict summation of the hypergeometric series is of little help for the numerical evaluation of the Coulomb functions, except in limited regions (see e.g. Bardin et al., 1972). The calculation algorithm adopted here is the continued fraction method due to Steed (Barnett et al., 1974), which is generally applicable for $x > x_{\rm TP}[\lambda]$. For sufficiently large values of x, however, we use an asymptotic expansion, which is much more effective. In the following, we quote the properties of Coulomb functions required for the derivation of Steed's algorithm.

The functions for successive λ-values are linked by recurrence relations (see e.g. Fröberg, 1955). The downward recursion, for decreasing orders, is

$$R_\lambda \, U_{\lambda-1} = S_\lambda \, U_\lambda + U'_\lambda, \tag{48}$$

$$U'_{\lambda-1} = S_\lambda \, U_{\lambda-1} - R_\lambda U_\lambda, \tag{49}$$

and the upward recursion is

$$R_{\lambda+1} \, U_{\lambda+1} = S_{\lambda+1} \, U_\lambda - U'_\lambda, \tag{50}$$

$$U'_{\lambda+1} = R_{\lambda+1} \, U_\lambda - S_{\lambda+1} \, U_{\lambda+1}. \tag{51}$$

Here again U_λ stands for either F_λ or G_λ, and the primes denote differentiation with respect to x. The coefficients for $\lambda \neq 0$ are

$$R_\lambda = \frac{1}{\lambda}\sqrt{\lambda^2 + \eta^2}, \qquad S_\lambda = \frac{\lambda}{x} + \frac{\eta}{\lambda}. \tag{52}$$

Combining the relations (50) and (51) we obtain

$$U_{\lambda+1} = \frac{S_{\lambda+1} + S_\lambda}{R_{\lambda+1}} \, U_\lambda - \frac{R_\lambda}{R_{\lambda+1}} \, U_{\lambda-1}. \tag{53}$$

Recursion relations are said to be stable when the quantities obtained from them do not decrease monotonously. Otherwise, there is a gradual loss of accuracy, due to the finite number of digits in the floating point representation, which may eventually invalidate the results. For $x < x_{\rm TP}[\lambda]$, F_λ decreases and G_λ increases for decreasing λ. Thus, the downward recursion for F_λ and the upward recursion for G_λ are stable. For $x > x_{\rm TP}[\lambda]$ the functions are always of the order of unity and, hence, both recursions are stable.

Further useful properties of the Coulomb functions are the Wronskian

$$\mathcal{W} \equiv F'_\lambda \, G_\lambda - F_\lambda \, G'_\lambda = 1 \tag{54}$$

and the relation

$$\mathcal{W}_\lambda \equiv F_\lambda \, G_{\lambda+1} - F_{\lambda+1} \, G_\lambda = 1/R_{\lambda+1}, \tag{55}$$

which follows from eq. (54) by eliminating the derivatives with the aid of eq. (50).

3.2 Steed's continued fraction method

Steed's method for the evaluation of Coulomb functions (Barnett et al., 1974) is based on the fact that, for $x \geq x_{\rm TP}[\lambda]$, the quantities

$$f_\lambda \equiv \frac{F'_\lambda}{F_\lambda} \qquad \text{and} \qquad p_\lambda + \mathrm{i}q_\lambda \equiv \frac{G'_\lambda + \mathrm{i}F'_\lambda}{G_\lambda + \mathrm{i}F_\lambda} \tag{56}$$

can be expressed as rapidly converging continued fractions. We evaluate these continued fractions by using the modified Wallis' algorithm described in appendix B. Equations (56) can then be solved for F'_λ, G_λ and G'_λ in terms of F_λ,

$$F'_\lambda = f_\lambda F_\lambda, \qquad G_\lambda = \frac{f_\lambda - p_\lambda}{q_\lambda} F_\lambda, \qquad G'_\lambda = \frac{p_\lambda\,(f_\lambda - p_\lambda) - q_\lambda^2}{q_\lambda} F_\lambda. \tag{57}$$

The absolute value of F_λ, i.e. the scaling factor in expressions (57), is determined from the Wronskian (54)

$$F_\lambda = \pm \left(\frac{q_\lambda}{(f_\lambda - p_\lambda)^2 + q_\lambda^2} \right)^{1/2}, \tag{58}$$

and, finally, its sign is obtained during the evaluation of f_λ (see below). Notice that

$$q_\lambda = \frac{1}{F_\lambda^2 + G_\lambda^2}. \tag{59}$$

3.2.1 Continued fraction for f_λ

Consider the sequences (n = 0,1,2, ...)

$$\begin{aligned} A_n &\equiv c_{11}\, F_{n+\lambda+1} + c_{12}\, G_{n+\lambda+1}, \\ B_n &\equiv c_{21}\, F_{n+\lambda+1} + c_{22}\, G_{n+\lambda+1}, \end{aligned} \tag{60}$$

where c_{ij} are four constants. According to eq. (53), A_n and B_n satisfy the recurrence relations

$$\begin{aligned} A_n &= A_{n-1}\, b_n + A_{n-2}\, a_n, \\ B_n &= B_{n-1}\, b_n + B_{n-2}\, a_n, \end{aligned} \tag{61}$$

with

$$a_n = -\frac{R_{n+\lambda}}{R_{n+\lambda+1}} = -\sqrt{\frac{(n+\lambda)^2 + \eta^2}{(n+\lambda+1)^2 + \eta^2}}\, \frac{n+\lambda+1}{n+\lambda} \tag{62}$$

and

$$b_n = \frac{S_{n+\lambda+1} + S_{n+\lambda}}{R_{n+\lambda+1}} = \frac{2(n+\lambda)+1}{\sqrt{(n+\lambda+1)^2 + \eta^2}} \left(\frac{n+\lambda+1}{x} + \frac{\eta}{n+\lambda} \right). \tag{63}$$

The constants c_{ij} are fixed so that

$$\begin{aligned} A_{-1} &= c_{11}\, F_\lambda + c_{12}\, G_\lambda = 1, \qquad & A_0 &= c_{11}\, F_{\lambda+1} + c_{12}\, G_{\lambda+1} = b_0, \\ B_{-1} &= c_{21}\, F_\lambda + c_{22}\, G_\lambda = 0, \qquad & B_0 &= c_{21}\, F_{\lambda+1} + c_{22}\, G_{\lambda+1} = 1. \end{aligned} \tag{64}$$

Using the properties (54) and (55) of the Coulomb functions, we obtain

$$\begin{aligned} c_{11} &= (G_{\lambda+1} - b_0\, G_\lambda)\, R_{\lambda+1}, & c_{12} &= (b_0\, F_\lambda - F_{\lambda+1})\, R_{\lambda+1}, \\ c_{21} &= -G_\lambda\, R_{\lambda+1}, & c_{22} &= F_\lambda\, R_{\lambda+1}. \end{aligned} \tag{65}$$

From eqs. (61) and (64), and making use of the results given in appendix B, it is clear that

$$\lim_{n\to\infty} \frac{A_n}{B_n} = b_0 + \frac{a_1}{b_1+}\, \frac{a_2}{b_2+}\, \frac{a_3}{b_3 + \cdots}.$$

On the other hand, since $F_{n+\lambda+1} \to 0$ and $G_{n+\lambda+1} \to \infty$ as $n \to \infty$, from eq. (60) it follows that

$$\lim_{n\to\infty} \frac{A_n}{B_n} = \frac{c_{12}}{c_{22}} = b_0 - \frac{F_{\lambda+1}}{F_\lambda}. \tag{66}$$

Therefore,

$$\frac{F_{\lambda+1}}{F_\lambda} = -\frac{a_1}{b_1+}\, \frac{a_2}{b_2+}\, \frac{a_3}{b_3 + \cdots}. \tag{67}$$

With the help of eq. (50), we eliminate $F_{\lambda+1}$ to obtain the following continued fraction for f_λ

$$f_\lambda = \frac{F'_\lambda}{F_\lambda} = S_{\lambda+1} + R_{\lambda+1} \frac{a_1}{b_1+}\, \frac{a_2}{b_2+}\, \frac{a_3}{b_3 + \cdots}. \tag{68}$$

The final step is to recast this continued fraction in a form that is more convenient for numerical evaluation. By means of the equivalence transformation (see appendix B)

$$c_n = x(n+\lambda)(n+\lambda+1)R_{n+\lambda+1} = x(n+\lambda)\sqrt{(n+\lambda+1)^2+\eta^2},$$

we obtain the transformed continued fraction

$$f_\lambda = S_{\lambda+1} + \frac{H_1}{K_1+}\, \frac{H_2}{K_2+}\, \frac{H_3}{K_3 + \cdots} \tag{69}$$

with

$$\begin{aligned} H_1 &= c_1 R_{\lambda+1} a_1 = -\,\frac{\lambda+2}{\lambda+1}\left[(\lambda+1)^2+\eta^2\right] x, \\ H_n &= c_{n-1} c_n a_n = -\left[(n+\lambda)^2-1\right]\left[(n+\lambda)^2+\eta^2\right] x^2, \qquad (n>1) \\ K_n &= c_n b_n = \left[2(n+\lambda)+1\right]\left[(n+\lambda)(n+\lambda+1)+\eta x\right]. \end{aligned} \tag{70}$$

The sign of F_λ, see eq. (58), is obtained during the calculation of f_λ using the following trick. We observe that as $n \to \infty$ the value of B_n, eq. (60), tends to $c_{22}\; G_{n+\lambda+1} = F_\lambda\; R_{\lambda+1}\; G_{n+\lambda+1}$ and $G_{n+\lambda+1} \to +\infty$. Therefore, the sign of F_λ is the sign of the n-th denominator B_n when the continued fraction has converged.

3.2.2 Continued fraction for $p_\lambda + \mathrm{i}q_\lambda$

The boundary conditions at infinity, eq. (45), suggest the replacement

$$G_\lambda + \mathrm{i}F_\lambda = y_\lambda(\eta, x)\exp(\mathrm{i}\theta_\lambda). \tag{71}$$

Then, the function $y_\lambda(\eta, x)$ satisfies the differential equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 2\mathrm{i}(1-\eta/x)\frac{\mathrm{d}}{\mathrm{d}x} + (\mathrm{i}\eta-\lambda)(\mathrm{i}\eta+\lambda+1)\frac{1}{x^2}\right) y_\lambda(\eta, x) = 0. \tag{72}$$

Introducing the variable $z \equiv (2\mathrm{i}x)^{-1}$, this equation transforms into the hypergeometric equation

$$\left(z^2\frac{\mathrm{d}^2}{\mathrm{d}z^2} + [z(a+b+1)-1]\frac{\mathrm{d}}{\mathrm{d}z} + ab\right) {}_2F_0(a,b;z) = 0 \tag{73}$$

with $a = \mathrm{i}\eta - \lambda$ and $b = \mathrm{i}\eta + \lambda + 1$. The solution with the required asymptotic behaviour ($\lim_{x\to\infty} y_\lambda(\eta, x) = 1$) is

$$y_\lambda(\eta, x) = {}_2F_0\left(\mathrm{i}\eta - \lambda, \mathrm{i}\eta + \lambda + 1; (2\mathrm{i}x)^{-1}\right) \tag{74}$$

$$= 1 + \frac{a\ b}{1!\ (2\mathrm{i}x)} + \frac{a(a+1)\ b(b+1)}{2!\ (2\mathrm{i}x)^2} + \cdots \tag{75}$$

The result (74) is exact; the series representation (75) is a known asymptotic form for $G_\lambda + \mathrm{i}F_\lambda$. This series is convergent only in the asymptotic sense, i.e. for relatively large values of x, and the summation must be terminated after the term with the smallest absolute magnitude (which normally gives a good estimate of the absolute error of the result).

From the differentiation property

$${}_2F_0'(a,b;z) \equiv \frac{\mathrm{d}\ {}_2F_0}{\mathrm{d}z} = ab\ {}_2F_0(a+1, b+1; z) \tag{76}$$

we find

$$p_\lambda + \mathrm{i}q_\lambda \equiv \frac{G_\lambda' + \mathrm{i}F_\lambda'}{G_\lambda + \mathrm{i}F_\lambda} = \mathrm{i}\left(1 - \frac{\eta}{x}\right) + \mathrm{i}\ \frac{ab}{2x^2}\ \frac{{}_2F_0(a+1, b+1; z)}{{}_2F_0(a, b; z)}. \tag{77}$$

Also, using (76) in eq. (73), dividing by ${}_2F_0'$ and rearranging we obtain

$$\frac{{}_2F_0(a,b;z)}{{}_2F_0(a+1,b+1;z)} = 1 - z(a+b+1) - z^2(a+1)(b+1)\ \frac{{}_2F_0(a+2,b+2;z)}{{}_2F_0(a+1,b+1;z)}.$$

Inverting this equation,

$$\frac{{}_2F_0(a+1,b+1;z)}{{}_2F_0(a,b;z)} = \frac{1}{1 - z(a+b+1) - z^2(a+1)(b+1)\ \dfrac{{}_2F_0(a+2,b+2;z)}{{}_2F_0(a+1,b+1;z)}},$$

and applying it repeatedly gives the continued fraction

$$\frac{{}_2F_0(a+1,b+1;z)}{{}_2F_0(a,b;z)} = \frac{1}{1 - z(a+b+1) -}\ \frac{z^2(a+1)(b+1)}{1 - z(a+b+3) -}\ \frac{z^2(a+2)(b+2)}{1 - z(a+b+5) - \cdots}.$$

Replacing the constants a and b, introducing $z = (2\mathrm{i}x)^{-1}$ and making an equivalence transformation with $c_n = 2x$ we get

$$\frac{{}_2F_0(a+1,b+1;z)}{{}_2F_0(a,b;z)} = \frac{2x}{2(x-\eta+\mathrm{i})+}\ \frac{(\mathrm{i}\eta-\lambda+1)(\mathrm{i}\eta+\lambda+2)}{2(x-\eta+2\mathrm{i})+}\ \frac{(\mathrm{i}\eta-\lambda+2)(\mathrm{i}\eta+\lambda+3)}{2(x-\eta+3\mathrm{i})+\cdots}$$

Finally, from eq. (77), we have

$$p_\lambda + \mathrm{i}q_\lambda = \frac{\mathrm{i}}{x}\left(K_0 + \frac{H_1}{K_1+}\,\frac{H_2}{K_2+}\,\frac{H_3}{K_3+\cdots}\right), \tag{78}$$

with

$$\begin{aligned} K_0 &= x - \eta, \\ K_n &= 2(x - \eta + \mathrm{i}n), \qquad (n \geq 1) \\ H_n &= (\mathrm{i}\eta - \lambda - 1 + n)(\mathrm{i}\eta + \lambda + n). \end{aligned} \tag{79}$$

The `FORTRAN 77` subroutine `FCOUL` calculates Coulomb functions and their derivatives for real η, real $\lambda > -1$ and real $x > 0$. It combines Steed's method with the asymptotic expansion (75) using double-precision arithmetic. If $x > x_{\mathrm{TP}}[\lambda]$, the asymptotic expansion is tentatively evaluated, and the relative error of the result is estimated from the magnitude of the term with the smallest absolute value. If this error is less than 10^{-15}, the Coulomb functions and their derivatives are delivered. Otherwise, Steed's algorithm is applied, using a maximum of 1000 iterations to evaluate the continued fractions. When these have converged, or when the 1000 iterations have been completed, the relative error of the resulting function values is determined from the differences between the last calculated convergents of the continued fractions. Among the results obtained with the two methods, the subroutine selects the ones with the lesser relative uncertainty. For $x > x_{\mathrm{TP}}[\lambda]$, the delivered values are usually accurate to 13 or 14 decimal figures.

For $x < x_{\mathrm{TP}}[\lambda]$, only Steed's method is applicable. In this case the accuracy of the algorithm worsens with decreasing x, due to the fact that G_λ and G'_λ increase without limit, while F_λ goes to zero. Thus, when x decreases, the ratio $|q_\lambda/p_\lambda|$ increases rapidly and, as a consequence, there is a gradual loss of significance. This difficulty is partially avoided by means of the following trick (Barnett, 1981). For $x < x_{\mathrm{TP}}[\lambda]$, the continued fraction for f_λ, eq. (69), is evaluated first and the downward recursions for F and F' (eqs. (48) and (49)) are applied to obtain the value of f_{L} for an index L which is less than 1 or such that x is larger than $x_{\mathrm{TP}}[\mathrm{L}]$, the turning point for the angular momentum L. The continued fraction for $p_{\mathrm{L}} + \mathrm{i}q_{\mathrm{L}}$ is then evaluated and the functions G_{L} and G'_{L} obtained from eqs. (57). The upward recursions for G and G' (eqs. (50) and (51)) are used to obtain G_λ and G'_λ. Finally, the Wronskian (54), together with the previously computed value of f_λ, determine F_λ and F'_λ. In this way, Coulomb functions can be calculated for all x larger than a value x_{crit} of the order of the turning point $x_{\mathrm{TP}}[0]$ for $\lambda = 0$. When $x \ll x_{\mathrm{TP}}[\lambda]$, the irregular functions may take exceedingly large values; to prevent computer overflows, the calculation is discontinued and an error code is returned to the `MAIN` program when $G_\lambda(\eta, x)$ is larger than $\sim 10^{30}$. For x-values less than x_{crit} or such that $G_\lambda(\eta, x) > 10^{30}$, regular Coulomb functions may be obtained by numerical integration of their differential equation (39) (e.g. by using the subroutine `SCH` included in the present package).

3.3 Bessel functions

The Bessel functions of the first kind, $J_\nu(x)$, and of the second kind, $Y_\nu(x)$, are the solutions of the differential equation (see e.g. Abramowitz and Stegun, 1974)

$$\frac{\mathrm{d}^2\,\omega_\nu(x)}{\mathrm{d}x^2} + \frac{1}{x}\,\frac{\mathrm{d}\,\omega_\nu(x)}{\mathrm{d}x} + \left(1 - \frac{\nu^2}{x^2}\right)\omega_\nu(x) = 0, \tag{80}$$

with the asymptotic behaviour

$$J_\nu(x) \sim \sqrt{\frac{2}{\pi x}}\,\sin\left(x - \nu\frac{\pi}{2} + \frac{\pi}{4}\right) \quad \text{and} \quad Y_\nu(x) \sim -\sqrt{\frac{2}{\pi x}}\,\cos\left(x - \nu\frac{\pi}{2} + \frac{\pi}{4}\right). \tag{81}$$

We remove the first derivative in eq. (80) with the transformation

$$\omega_\nu(x) = x^{-1/2}\,\mathrm{w}_\nu(x), \tag{82}$$

which yields

$$\frac{\mathrm{d}^2\,\mathrm{w}_\nu(x)}{\mathrm{d}x^2} + \left(1 - \frac{\nu^2 - 1/4}{x^2}\right)\mathrm{w}_\nu(x) = 0. \tag{83}$$

This equation is of the form (40) with $\eta = 0$ and $\lambda = \nu - 1/2$ and, therefore, for $\nu > -1/2$,

$$J_\nu(x) = \sqrt{\frac{2}{\pi x}}\,F_{\nu-1/2}\,(0,x) \qquad \text{and} \qquad Y_\nu(x) = -\sqrt{\frac{2}{\pi x}}\,G_{\nu-1/2}\,(0,x). \tag{84}$$

Subroutine `FCOUL` can then be used to compute Bessel functions of orders $\nu > -1/2$, and their derivatives, for $x > 0$ to high accuracy. The idea of employing Steed's algorithm to calculate Bessel functions is due to Barnett (1981).

The spherical Bessel functions of the first kind, $j_\nu(x)$, and of the second kind, $n_\nu(x)$, are defined by[2]

$$\begin{aligned} j_\nu(x) &= \sqrt{\frac{\pi}{2x}}\,J_{\nu+1/2}\,(x) = \frac{1}{x}F_\nu\,(0,x), \\ n_\nu(x) &= \sqrt{\frac{\pi}{2x}}\,Y_{\nu+1/2}\,(x) = -\frac{1}{x}G_\nu\,(0,x). \end{aligned} \tag{85}$$

They satisfy the differential equation

$$\frac{\mathrm{d}^2\,\omega_\nu(x)}{\mathrm{d}x^2} + \frac{2}{x}\,\frac{\mathrm{d}\,\omega_\nu(x)}{\mathrm{d}x} + \left(1 - \frac{\nu(\nu+1)}{x^2}\right)\omega_\nu(x) = 0, \tag{86}$$

and have the following asymptotic behaviour

$$j_\nu(x) \sim \frac{1}{x}\,\sin\left(x - \nu\frac{\pi}{2}\right) \qquad \text{and} \qquad n_\nu(x) \sim -\frac{1}{x}\,\cos\left(x - \nu\frac{\pi}{2}\right). \tag{87}$$

[2]The functions $j_\nu(x)$ and $n_\nu(x)$ are also known as the spherical Bessel and Neumann functions, respectively.

Spherical Bessel functions of integer order ($\nu = \ell \geq 0$) are used by `RADIAL` to normalize free states for finite-range fields (see section 6). Although these functions could be calculated by means of subroutine `FCOUL`, it is faster to generate them from the exact expressions

$$j_0(x) = \frac{\sin x}{x} \qquad \text{and} \qquad n_0(x) = -\frac{\cos x}{x}, \tag{88}$$

using the recurrence relations satisfied by $j_\ell(x)$ and $n_\ell(x)$ (which may be easily derived from those of the Coulomb functions). Notice that the upward recursion for $j_\ell(x)$ and $x < \ell$ is unstable; in this case, Miller's downward recursion method (Abramowitz and Stegun, 1974) can be applied. This is the procedure adopted in function `BESJN`, which delivers accurate values of spherical Bessel and Neumann functions of integer order for any $x > 0$.

3.4 Dirac-Coulomb functions

The free-state ($E > 0$) solution of Dirac's equation for the Coulomb field (38) is usually obtained by directly solving the coupled pair of first order radial differential equations (16)

$$\begin{aligned} \frac{\mathrm{d}\, u_\kappa^{(\mathrm{u})}}{\mathrm{d}r} &= -\frac{\kappa}{r}\, u_\kappa^{(\mathrm{u})} - \frac{W + Mc^2}{c\hbar}\, u_\kappa^{(\mathrm{l})} + \frac{\zeta}{r}\, u_\kappa^{(\mathrm{l})}, \\ \frac{\mathrm{d}\, u_\kappa^{(\mathrm{l})}}{\mathrm{d}r} &= \frac{W - Mc^2}{c\hbar}\, u_\kappa^{(\mathrm{u})} - \frac{\zeta}{r}\, u_\kappa^{(\mathrm{u})} + \frac{\kappa}{r}\, u_\kappa^{(\mathrm{l})}, \end{aligned} \tag{89}$$

where $W \equiv E + Mc^2$ is the total energy,

$$\zeta \equiv \frac{Ze^2}{\hbar c} = Z\alpha, \tag{90}$$

and $u_\kappa^{(\mathrm{u})}$ and $u_\kappa^{(\mathrm{l})}$ stand for the upper and lower spinor radial functions respectively. The quantity $\alpha \equiv e^2/(\hbar c) \simeq 1/137$ is the fine-structure constant.

The solutions $u_\kappa^{(\mathrm{u})}$, $u_\kappa^{(\mathrm{l})}$ of eqs. (89) are expressable as linear combinations of two confluent hypergeometric functions with complex arguments (Rose, 1961; Greiner, 1990). However, in order to arrive at this result, it is necessary to write the radial functions in a special form, which is only justified from a previous knowledge of the character of the solution. Moreover, to obtain the form that corresponds with the non-relativistic limit it is necessary to perform intricate manipulations using the properties of the confluent hypergeometric functions. Finally, the numerical evaluation of the irregular Dirac-Coulomb functions is a difficult problem that, to our knowledge, is still unsolved except for large radii, where the asymptotic expansions of the confluent hypergeometric functions converge to the desired accuracy.

In the present calculations, we use an alternative method that is free from all these difficulties. The method is based on the, not widely known, fact that eqs. (89) can

be transformed to a pair of equations of the form (40) with non-integer λ's[3]. The transformation shows, in a natural way, that the regular and irregular solutions of the Dirac equation (89) are linear combinations of Schrödinger-Coulomb functions. Our transformation is similar to one described by Kolsrud (1966), who only considered the regular solutions. We have generalized the final steps of the derivation so as to also include the irregular solution. This transformation has been formulated in a different way by Auvil and Brown (1978), who applied it to bound states of the hydrogen atom.

Introducing the dimensionless variable $x = kr$, where k is the relativistic wave number (eq. (20))

$$k = \frac{\sqrt{W^2 - M^2c^4}}{\hbar c}, \tag{91}$$

eq. (89) can be written in the following matrix form:

$$\begin{pmatrix} \dfrac{\mathrm{d}}{\mathrm{d}x} + \dfrac{\kappa}{x} & \dfrac{W + Mc^2}{k\hbar c} - \dfrac{\zeta}{x} \\ -\dfrac{W - Mc^2}{k\hbar c} + \dfrac{\zeta}{x} & \dfrac{\mathrm{d}}{\mathrm{d}x} - \dfrac{\kappa}{x} \end{pmatrix} u_\kappa(x) = 0, \qquad u_\kappa(x) \equiv \begin{pmatrix} u_\kappa^{(\mathrm{u})}(r) \\ u_\kappa^{(\mathrm{l})}(r) \end{pmatrix}, \tag{92}$$

or, in terms of the Pauli matrices (11),

$$\left[\frac{\mathrm{d}}{\mathrm{d}x} + \frac{1}{x}\left(\kappa\sigma_3 - \mathrm{i}\zeta\sigma_2\right) + \frac{\mathrm{i}}{k\hbar\, c}\left(W\sigma_2 - \mathrm{i}Mc^2\sigma_1\right)\right] u_\kappa(x) = 0. \tag{93}$$

From the structure of this equation, it is natural to define the matrices

$$\Xi \equiv \frac{1}{k\hbar\, c}\left(W\sigma_2 - \mathrm{i}Mc^2\sigma_1\right) = \frac{1}{k\hbar\, c}\begin{pmatrix} 0 & -\mathrm{i}\,(W + Mc^2) \\ \mathrm{i}\,(W - Mc^2) & 0 \end{pmatrix} \tag{94}$$

and

$$\Lambda \equiv \frac{1}{\lambda}\left(\kappa\sigma_3 - \mathrm{i}\zeta\sigma_2\right) = \frac{1}{\lambda}\begin{pmatrix} \kappa & -\zeta \\ \zeta & -\kappa \end{pmatrix}, \tag{95}$$

with

$$\lambda \equiv \sqrt{\kappa^2 - \zeta^2}. \tag{96}$$

The global factors in these matrices are such that

$$\Xi^2 = \Lambda^2 = 1 \qquad \text{and} \qquad \Lambda\,\Xi + \Xi\,\Lambda = -\frac{2\mathrm{i}\,\zeta\, W}{\lambda\, k\hbar\, c}. \tag{97}$$

Equation (93) can now be written in the more compact form

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\lambda}{x}\,\Lambda + \mathrm{i}\,\Xi\right) u_\kappa = 0. \tag{98}$$

[3]However, it is well known that the Klein-Gordon equation (also called the relativistic Schrödinger equation) for a Coulomb potential can be reduced to a form equivalent to eq. (40) (see Schiff, 1968).

Following Kolsrud (1966), this equation is "squared" as

$$\frac{\mathrm{d}^2 u_\kappa}{\mathrm{d}x^2} = \frac{\mathrm{d}}{\mathrm{d}x}\left(-\frac{\lambda}{x}\Lambda - \mathrm{i}\,\Xi\right) u_\kappa = \left(-\frac{\lambda}{x}\Lambda - \mathrm{i}\,\Xi\right)^2 u_\kappa. \tag{99}$$

Using the properties (97) of the Ξ and Λ matrices, and introducing the relativistic Sommerfeld parameter (cf. eq. (41))

$$\eta = \frac{\zeta W}{k\hbar\, c} = \zeta\,\frac{c}{v} = \frac{Ze^2}{\hbar v}, \tag{100}$$

we obtain

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 1 - \frac{2\eta}{x} - \frac{\lambda(\lambda+\Lambda)}{x^2}\right) u_\kappa = 0, \tag{101}$$

which has a clear resemblance with the non-relativistic equation (40). An even closer similarity is obtained by introducing a linear transformation C that diagonalizes Λ,

$$C\,\Lambda\,C^{-1} = \sigma_3. \tag{102}$$

The required transformation is

$$C = \Lambda + \sigma_3 = \frac{1}{\lambda}\begin{pmatrix} \kappa+\lambda & -\zeta \\ \zeta & -\kappa-\lambda \end{pmatrix}, \qquad C^{-1} = \frac{\lambda}{2(\kappa+\lambda)}C, \tag{103}$$

and the transformed second-order equation reads

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 1 - \frac{2\eta}{x} - \frac{\lambda(\lambda+\sigma_3)}{x^2}\right) C u_\kappa = 0. \tag{104}$$

It then follows that

$$C u_\kappa = \begin{pmatrix} q_1\, U_\lambda(\eta, x) \\ q_2\, U_{\lambda-1}(\eta, x) \end{pmatrix}, \tag{105}$$

where the functions $U_\lambda(\eta, x)$ are solutions of the equation (40), i.e. the usual Schrödinger-Coulomb functions, with the indicated parameters. This is the essential result obtained by Kolsrud (1966) and by Auvil and Brown (1978).

The ratio of the coefficients q_1 and q_2 is determined by transforming the first-order equation (98),

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\lambda}{x}\,\sigma_3 + \mathrm{i}\,C\,\Xi\,C^{-1}\right) C u_\kappa = 0. \tag{106}$$

A simple calculation shows that

$$\mathrm{i}\,C\,\Xi\,C^{-1} = \frac{1}{\lambda\, k\hbar\, c}\left(-\lambda\, Mc^2\,\sigma_1 - \kappa\, W\,\mathrm{i}\,\sigma_2 + \zeta\, W\sigma_3\right),$$

and eq. (106) takes the form

$$\begin{pmatrix} \dfrac{\mathrm{d}}{\mathrm{d}x} + \dfrac{\lambda}{x} + \dfrac{\eta}{\lambda} & -\dfrac{1}{\lambda\, k\hbar\, c}\left(\lambda\, Mc^2 + \kappa\, W\right) \\ -\dfrac{1}{\lambda\, k\hbar\, c}\left(\lambda\, Mc^2 - \kappa\, W\right) & \dfrac{\mathrm{d}}{\mathrm{d}x} - \dfrac{\lambda}{x} - \dfrac{\eta}{\lambda} \end{pmatrix} \begin{pmatrix} q_1\, U_\lambda(\eta, x) \\ q_2\, U_{\lambda-1}(\eta, x) \end{pmatrix} = 0. \tag{107}$$

Using the recurrence relations (48) and (50) of the Coulomb functions, we get the couple of linearly dependent equations

$$\begin{aligned}\sqrt{\lambda^2+\eta^2}\;k\hbar\,c\;q_1-\left(\lambda\,Mc^2+\kappa\,W\right)q_2 &= 0,\\ \left(\lambda\,Mc^2-\kappa\,W\right)q_1+\sqrt{\lambda^2+\eta^2}\;k\hbar\,c\;q_2 &= 0,\end{aligned}\tag{108}$$

which give

$$\frac{q_1}{q_2}=\frac{\sqrt{\lambda^2+\eta^2}\;k\hbar\,c}{-\left(\lambda\,Mc^2-\kappa\,W\right)}.\tag{109}$$

Thus,

$$\begin{pmatrix} u_\kappa^{(\mathrm{u})}(\eta,x)\\ u_\kappa^{(\mathrm{l})}(\eta,x)\end{pmatrix}=C^{-1}\begin{pmatrix} N\sqrt{\lambda^2+\eta^2}\;k\hbar\,c\;U_\lambda(\eta,x)\\ -N\;\left(\lambda\,Mc^2-\kappa\,W\right)\;U_{\lambda-1}(\eta,x)\end{pmatrix},\tag{110}$$

and we obtain the following form of the Dirac-Coulomb radial functions

$$\begin{aligned}u_\kappa^{(\mathrm{u})}(\eta,x)&=N\left[(\kappa+\lambda)\sqrt{\lambda^2+\eta^2}\;k\hbar\,c\;U_\lambda(\eta,x)+\zeta\left(\lambda\,Mc^2-\kappa\,W\right)\;U_{\lambda-1}(\eta,x)\right],\\ u_\kappa^{(\mathrm{l})}(\eta,x)&=N\left[\zeta\sqrt{\lambda^2+\eta^2}\;k\hbar\,c\;U_\lambda(\eta,x)+(\kappa+\lambda)\left(\lambda\,Mc^2-\kappa\,W\right)\;U_{\lambda-1}(\eta,x)\right],\end{aligned}\tag{111}$$

where N is a normalization constant. Finally, this constant is fixed by requiring that $u_\kappa^{(\mathrm{u})}(\eta,x)$ oscillates asymptotically with unit amplitude.

We recall that the form (111) applies to *both* the regular and irregular Dirac-Coulomb functions, which will be denoted as $f_\kappa^{(\mathrm{u,l})}(x)$ and $g_\kappa^{(\mathrm{u,l})}(x)$, respectively. Considering this, and the asymptotic behaviour (45) of the Coulomb functions, we have

$$g_\kappa^{(\mathrm{u})}(x)+\mathrm{i}f_\kappa^{(\mathrm{u})}(x)\sim N\left[(\kappa+\lambda)\sqrt{\lambda^2+\eta^2}\;k\hbar\,c\;\exp(\mathrm{i}\Delta\theta)+\zeta\left(\lambda\,Mc^2-\kappa\,W\right)\right]\exp(\mathrm{i}\theta_{\lambda-1}).$$

From the definition (46), using the properties of the Γ function, we find that the phase difference $\Delta\theta\equiv\theta_\lambda-\theta_{\lambda-1}$ is

$$\Delta\theta=-\frac{\pi}{2}+\arg\frac{\Gamma(\lambda+1+\mathrm{i}\eta)}{\Gamma(\lambda+\mathrm{i}\eta)}=-\frac{\pi}{2}+\arg(\lambda+\mathrm{i}\eta),\tag{112}$$

and

$$\exp(\mathrm{i}\Delta\theta)=\frac{\eta-\mathrm{i}\lambda}{\sqrt{\lambda^2+\eta^2}}.\tag{113}$$

Therefore,

$$\begin{aligned}g_\kappa^{(\mathrm{u})}(x)+\mathrm{i}f_\kappa^{(\mathrm{u})}(x) &\sim N\left[(\kappa+\lambda)\;k\hbar\,c\;(\eta-\mathrm{i}\,\lambda)+\zeta\left(\lambda\,Mc^2-\kappa\,W\right)\right]\exp(\mathrm{i}\theta_{\lambda-1})\\ &= N\lambda\left[\zeta\left(W+Mc^2\right)-\mathrm{i}\;(\kappa+\lambda)\;k\hbar\,c\right]\exp(\mathrm{i}\theta_{\lambda-1}).\end{aligned}\tag{114}$$

We obtain the desired asymptotic behaviour by setting

$$N=\pm\,\frac{1}{\lambda}\;\left[\zeta^2\left(W+Mc^2\right)^2+(\kappa+\lambda)^2(k\hbar\,c)^2\right]^{-1/2},\tag{115}$$

so that

$$g_\kappa^{(\mathrm{u})}(x) + \mathrm{i} f_\kappa^{(\mathrm{u})}(x) \sim \pm \exp\left[\mathrm{i}\left(\nu + \theta_{\lambda-1}\right)\right] \tag{116}$$

with

$$\nu = \arg\left[\zeta\left(W + Mc^2\right) - \mathrm{i}\left(\kappa + \lambda\right) k\hbar\, c\right]. \tag{117}$$

This completes the derivation of the normalized Dirac-Coulomb radial functions. The simplicity of this last step is in marked contrast with the elaborate manipulations needed to obtain the normalization constant in the standard derivation (see e.g. Rose, 1961; Greiner, 1990).

As a matter of fact, there is a physically irrelevant sign ambiguity in expression (115). The "good" sign is obtained by requiring that, in the non-relativistic limit $c \to \infty$ ($E \ll Mc^2$, $\lambda \to |\kappa|$), the small radial functions $u_\kappa^{(\mathrm{l})}$ vanish and the large functions reduce to the non-relativistic Coulomb functions

$$f_\kappa^{(\mathrm{u})}(x) \xrightarrow{\text{n.r.}} F_\ell(\eta, x), \qquad g_\kappa^{(\mathrm{u})}(x) \xrightarrow{\text{n.r.}} G_\ell(\eta, x), \tag{118}$$

where ℓ stands for the orbital angular momentum quantum number ($\ell = \kappa$ if $\kappa > 0$ and $\ell = -\kappa - 1$ if $\kappa < 0$). This is accomplished by taking the minus sign in eq. (115) when ζ *and* κ are negative, and the plus sign otherwise.

Asymptotically, the upper-component radial functions behave as

$$f_\kappa^{(\mathrm{u})}(x) \sim \sin\,\phi_\kappa \qquad \text{and} \qquad g_\kappa^{(\mathrm{u})}(x) \sim \cos\,\phi_\kappa, \tag{119}$$

with

$$\phi_\kappa = \nu + \theta_{\lambda-1} - \mathcal{S}_{\zeta,\kappa}\,\pi, \tag{120}$$

where, according to our sign convention, $\mathcal{S}_{\zeta,\kappa} = 1$ if $\zeta < 0$ and $\kappa < 0$, and $= 0$ otherwise. We can write this last expression in the more conventional form

$$\phi_\kappa = x - \ell\frac{\pi}{2} - \eta\,\ln 2x + \Delta_\kappa. \tag{121}$$

The Dirac-Coulomb phase shift is

$$\Delta_\kappa \equiv \nu - (\lambda - \ell - 1)\frac{\pi}{2} + \arg\Gamma(\lambda + \mathrm{i}\eta) - \mathcal{S}_{\zeta,\kappa}\,\pi. \tag{122}$$

With the adopted sign convention, Dirac-Coulomb phase shifts vanish in the zero field limit. The asymptotic behaviour of the lower component functions is easily obtained by means of the first of the Dirac equations (89),

$$u_\kappa^{(\mathrm{l})} \sim -\frac{\hbar k\, c}{W + Mc^2}\,\frac{\mathrm{d}u_\kappa^{(\mathrm{u})}(x)}{\mathrm{d}x} = -\sqrt{\frac{W - Mc^2}{W + Mc^2}}\,\frac{\mathrm{d}u_\kappa^{(\mathrm{u})}(x)}{\mathrm{d}x}, \tag{123}$$

which gives

$$f_\kappa^{(\mathrm{l})}(x) \sim -\sqrt{\frac{W - Mc^2}{W + Mc^2}}\,\cos\,\phi_\kappa \qquad \text{and} \qquad g_\kappa^{(\mathrm{l})}(x) \sim \sqrt{\frac{W - Mc^2}{W + Mc^2}}\,\sin\,\phi_\kappa. \tag{124}$$

In the limit of zero field strength ($\zeta \to 0, \lambda = |\kappa|$), we find

$$\begin{aligned} u_\kappa^{(\mathrm{u})}(x) &= U_\kappa(0,x), \qquad & u_\kappa^{(\mathrm{l})}(x) &= -\sqrt{\frac{W-Mc^2}{W+Mc^2}}\, U_{\kappa-1}(0,x) \qquad & \text{if } \kappa > 0, \\ u_\kappa^{(\mathrm{u})}(x) &= U_{-\kappa-1}(0,x), \qquad & u_\kappa^{(\mathrm{l})}(x) &= \sqrt{\frac{W-Mc^2}{W+Mc^2}}\, U_{-\kappa}(0,x) \qquad & \text{if } \kappa < 0, \end{aligned} \tag{125}$$

which, with the aid of the relations (85), lead to the familiar result that free particle Dirac radial functions are spherical Bessel functions (see e.g. Rose, 1961, p. 161).

The `RADIAL` package includes the subroutine `DCOUL`, which computes the Dirac-Coulomb functions $f_\kappa^{(\mathrm{u,l})}(r)$ and $g_\kappa^{(\mathrm{u,l})}(r)$ by using the values of the Schrödinger-Coulomb functions delivered by subroutine `FCOUL`.

4 Power series solution of the radial equations

In the following sections, and in the computer code, we use generalized atomic units. In these units, the reduced Planck constant $\hbar$, the absolute value of the electron charge e and the mass M of the considered particle are taken as unity. The atomic units of energy and length are given by $E_0 = Me^4/\hbar^2$ and $a_0 = \hbar^2/(Me^2)$ respectively. The speed of light in vacuum is $c = 137.036$, i.e. the inverse of the fine-structure constant. For electrons and positrons, the units of energy and length are the Hartree energy ($E_0 = 27.2114$ eV) and the Bohr radius ($a_0 = 0.529177$ Å). In these units, the radial Schrödinger eq. (4) takes the form

$$-\frac{1}{2}\frac{\mathrm{d}^2P}{\mathrm{d}r^2} + \left[V(r) + \frac{\ell(\ell+1)}{2r^2}\right] P = EP, \tag{126}$$

and the radial Dirac eqs. (16) read

$$\begin{aligned} \frac{\mathrm{d}P}{\mathrm{d}r} &= -\frac{\kappa}{r}\,P \quad - \frac{E-V+2c^2}{c}\,Q, \\ \frac{\mathrm{d}Q}{\mathrm{d}r} &= \frac{E-V}{c}\,P \qquad + \frac{\kappa}{r}\,Q. \end{aligned} \tag{127}$$

Let us assume that the values $\mathcal{V}_i \equiv r_i V(r_i)$ have been given for a grid of points $r_1 = 0 < r_2 < \ldots < r_{\mathrm{NV}}$. In the numerical routines, the function $\mathcal{V}(r)$ is approximated by the natural cubic spline (see appendix A) which interpolates the input values, i.e. by a piecewise cubic polynomial

$$\mathcal{V}(r) = v_0^{(i)} + v_1^{(i)} r + v_2^{(i)} r^2 + v_3^{(i)} r^3 \qquad \text{if } \; r_i \le r < r_{i+1} \tag{128}$$

with continuous first and second derivatives. Fields having a finite number of discontinuities are dealt with by using different splines in each continuous region. In this case, the locations of the discontinuities are specified by simply introducing the two values of

the potential for the *same* point; i.e. when $r_i = r_{i+1}$ the adopted piecewise spline takes the values $\mathcal{V}_i$ and $\mathcal{V}_{i+1}$ to the left and right of r_i respectively. The only requirements on the spacing of the grid points are: 1) the interpolation errors introduced by the spline approximation (128) have to be small and 2) the last grid point $r_{\rm NV}$ should be selected such that the potential function has reached its (constant) asymptotic value, i.e. $\mathcal{V}(r) = \mathcal{V}(r_{\rm NV})$ for $r > r_{\rm NV}$. In fact, this last condition is implicitly assumed by `RADIAL`, which sets $\mathcal{V}(r) = \mathcal{V}(r_{\rm NV})$ for $r > r_{\rm NV}$. Notice that it is not necessary to use uniform grids.

4.1 Schrödinger equation

We consider that the values of the radial function and its first derivative at a given point $r_{\rm a}$ have already been computed. What we want to do is to evaluate the functions $P(r)$ and $P'(r) \equiv {\rm d}P/{\rm d}r$ in the interval between $r_{\rm a}$ and $r_{\rm b}$, where the field function $\mathcal{V}(r)$ is given by

$$\mathcal{V}(r) \equiv rV(r) = v_0 + v_1 r + v_2 r^2 + v_3 r^3. \tag{129}$$

Introducing the new variable

$$x \equiv (r - r_{\rm a})/h, \qquad h \equiv r_{\rm b} - r_{\rm a}, \tag{130}$$

the radial equation (126) transforms to

$$(r_{\rm a} + hx)^2 \frac{{\rm d}^2\mathcal{P}}{{\rm d}x^2} - h^2\mathcal{U}(x)\mathcal{P} = 0, \tag{131}$$

with

$$\mathcal{P}(x) \equiv P(r) \tag{132}$$

and

$$\mathcal{U}(x) \equiv 2r^2[V(r) - E] + \ell(\ell+1) = u_0 + u_1 x + u_2 x^2 + u_3 x^3 + u_4 x^4, \tag{133}$$

where

$$\begin{aligned}
u_0 &= \ell(\ell+1) + 2v_0 r_{\rm a} + 2(v_1 - E) r_{\rm a}^2 + 2v_2 r_{\rm a}^3 + 2v_3 r_{\rm a}^4, \\
u_1 &= 2\left[v_0 + 2(v_1 - E) r_{\rm a} + 3v_2 r_{\rm a}^2 + 4v_3 r_{\rm a}^3\right] h, \\
u_2 &= 2\left[(v_1 - E) + 3v_2 r_{\rm a} + 6v_3 r_{\rm a}^2\right] h^2, \\
u_3 &= 2\left(v_2 + 4v_3 r_{\rm a}\right) h^3, \\
u_4 &= 2v_3 h^4.
\end{aligned} \tag{134}$$

The radial function $\mathcal{P}(x)$ is now expanded as a power series in x

$$\mathcal{P}(x) = \sum_{n=0}^{\infty} a_n x^n. \tag{135}$$

Introducing (135) in (131) we obtain the following recurrence relation for the coefficients in the series

$$a_n = \frac{h}{n(n-1)r_\mathrm{a}}\left[-2(n-1)(n-2)a_{n-1} + \frac{h}{r_\mathrm{a}}\left\{\Big(u_0 - (n-2)(n-3)\Big)\,a_{n-2} + u_1 a_{n-3} + u_2 a_{n-4} + u_3 a_{n-5} + u_4 a_{n-6}\right\}\right], \tag{136}$$

which determines the values of all the a_n from the boundary conditions

$$a_0 = P(r_\mathrm{a}), \qquad a_1 = hP'(r_\mathrm{a}). \tag{137}$$

Generally we will only be interested in the values of $P(r)$ and $P'(r)$ at the end point r_b ($x = 1$):

$$P(r_\mathrm{b}) = \mathcal{P}(1) = \sum_{n=0}^{\infty} a_n, \qquad P'(r_\mathrm{b}) = h^{-1}\mathcal{P}'(1) = h^{-1}\sum_{n=0}^{\infty} n a_n. \tag{138}$$

In the numerical evaluation, the series $\mathcal{P}(1)$ and $\mathcal{P}'(1)$ may be summed *exactly*, i.e. we can add enough terms to ensure that the relative error in the sum is smaller than a certain value ϵ ($\ll 1$), which should be of the order of 10^{-15} to get the optimum accuracy attainable with double-precision arithmetic. We adopt the following convergence criteria: the summation of series (138) is stopped when the last added term, a_j, satisfies the conditions

$$|a_j| < \epsilon \max\left\{\left|\sum_{n=0}^{j} a_n\right|, \frac{1}{j}\left|\sum_{n=0}^{j} n a_n\right|\right\} \tag{139a}$$

and, at the same time,

$$\left|r_\mathrm{b}^2\mathcal{P}''(1) - h^2\mathcal{U}(1)\mathcal{P}(1)\right| < \epsilon \max\left\{\left|\mathcal{P}(1)\right|, \left|\mathcal{P}'(1)\right|\right\}, \tag{139b}$$

so that the function $\mathcal{P}(x)$ fulfills differential equation (131) in the considered interval with the required accuracy. Notice that in order to check this last condition it is necessary to also sum the series for $\mathcal{P}''(1)$.

When $r_\mathrm{a} = r_1 = 0$, i.e. to start the solution from the centre of force, we must proceed in a slightly different way. In this case we take

$$\mathcal{P}(x) = x^s \sum_{n=0}^{\infty} a_n x^n. \tag{140}$$

Introducing (140) in (131) we get the recurrence relation

$$a_n = \frac{u_1 a_{n-1} + u_2 a_{n-2} + u_3 a_{n-3} + u_4 a_{n-4}}{(s+n)(s+n-1) - u_0}. \tag{141}$$

For $n = 0$, we must have $a_0 \neq 0$ and hence

$$s(s-1) = u_0 = \ell(\ell+1). \tag{142}$$

The regular solution is obtained for $s = \ell + 1$. The radial function at r_2 is renormalized in such a way that

$$P(r_2) = 1, \qquad P'(r_2) = \mathcal{P}'(1)/\mathcal{P}(1). \tag{143}$$

In the summation of series (140) we use the convergence criteria given by eqs. (139).

4.2 Dirac equation

The Dirac equation (127) is solved in a similar way. We assume that the values of the radial functions P and Q at the point $r_{\rm a}$ are known. We wish to determine these functions in the interval between $r_{\rm a}$ and $r_{\rm b}$, where the field function $\mathcal{V}(r)$ is again given by (129).

After changing to the new variable x, eq. (130), the radial equations (127) are written in the form

$$\begin{aligned}(r_{\rm a}+hx)\mathcal{P}' - \sigma|\kappa|h\mathcal{P} - \mathcal{U}h\mathcal{Q} + 2ch(r_{\rm a}+hx)\mathcal{Q} = 0,\\ (r_{\rm a}+hx)\mathcal{Q}' + \sigma|\kappa|h\mathcal{Q} + \mathcal{U}h\mathcal{P} = 0,\end{aligned} \tag{144}$$

with

$$\mathcal{P}(x) \equiv P(r), \qquad \mathcal{Q}(x) \equiv Q(r), \tag{145}$$

$\sigma = -{\rm sgn}(\kappa)$, and

$$\mathcal{U}(x) \equiv \frac{r[V(r)-E]}{c} = u_0 + u_1 x + u_2 x^2 + u_3 x^3, \tag{146}$$

where

$$\begin{aligned} u_0 &= c^{-1}\left[v_0 + (v_1 - E)r_{\rm a} + v_2 r_{\rm a}^2 + v_3 r_{\rm a}^3\right],\\ u_1 &= c^{-1}\left[(v_1 - E) + 2v_2 r_{\rm a} + 3v_3 r_{\rm a}^2\right]h,\\ u_2 &= c^{-1}\left[v_2 + 3v_3 r_{\rm a}\right]h^2,\\ u_3 &= c^{-1}v_3 h^3.\end{aligned} \tag{147}$$

Introducing the series expansions

$$\mathcal{P}(x) = \sum_{n=0}^{\infty} a_n x^n, \qquad \mathcal{Q}(x) = \sum_{n=0}^{\infty} b_n x^n \tag{148}$$

in (144), we find the following recurrence relations for the coefficients

$$\begin{aligned} a_n &= \frac{h}{nr_{\rm a}}\left[-(n-1-\sigma|\kappa|)a_{n-1}\right.\\ &\quad \left. + (u_0 - 2cr_{\rm a})b_{n-1} + (u_1 - 2ch)b_{n-2} + u_2 b_{n-3} + u_3 b_{n-4}\right],\\ b_n &= -\frac{h}{nr_{\rm a}}\left[u_0 a_{n-1} + (n-1+\sigma|\kappa|)b_{n-1} + u_1 a_{n-2} + u_2 a_{n-3} + u_3 a_{n-4}\right].\end{aligned} \tag{149}$$

Using these relations and the boundary conditions

$$a_0 = P(r_{\rm a}), \qquad b_0 = Q(r_{\rm a}), \tag{150}$$

the coefficients a_n and b_n are completely determined. The values of $P(r)$ and $Q(r)$ at the end point $r_{\rm b}$ ($x = 1$) are given by

$$P(r_{\rm b}) = \mathcal{P}(1), \qquad Q(r_{\rm b}) = \mathcal{Q}(1). \tag{151}$$

In the numerical evaluation of the series $\mathcal{P}(1)$ and $\mathcal{Q}(1)$ we adopt a convergence criterion similar to (139). The summation is stopped when the last added terms, a_j and b_j, satisfy the conditions

$$\max\left\{|a_j|\,,|b_j|\right\} < \epsilon \max\left\{\left|\sum_{n=0}^{j} a_n\right|\,,\left|\sum_{n=0}^{j} b_n\right|\right\} \tag{152a}$$

and, at the same time,

$$\begin{aligned}\max\Big\{&\left|r_{\rm b}\mathcal{P}'(1)-\sigma|\kappa|h\mathcal{P}(1)-(\mathcal{U}-2cr_{\rm b})\,h\mathcal{Q}(1)\right|,\\ &\left|r_{\rm b}\mathcal{Q}'(1)+\sigma|\kappa|h\mathcal{Q}(1)+\mathcal{U}h\mathcal{P}(1)\right|\Big\} \;<\; \epsilon\max\left\{|\mathcal{P}(1)|\,,|\mathcal{Q}(1)|\right\}.\end{aligned} \tag{152b}$$

In order to check this last condition it is necessary to also sum the series for $\mathcal{P}'(1)$ and $\mathcal{Q}'(1)$.

As in the case of the Schrödinger equation, special series expansions must be used to start the solutions at $r_{\rm a} = r_1 = 0$. We take

$$\mathcal{P}(x) = x^s \sum_{n=0}^{\infty} a_n x^n, \qquad \mathcal{Q}(x) = x^{s+t} \sum_{n=0}^{\infty} b_n x^n. \tag{153}$$

Introducing (153) in (144) we get

$$\begin{aligned}&(s+n-\sigma|\kappa|)a_n - u_0 b_{n-t} - (u_1-2ch)b_{n-t-1} - u_2 b_{n-t-2} - u_3 b_{n-t-3} = 0,\\ &(s+n+\sigma|\kappa|)b_{n-t} + u_0 a_n + u_1 a_{n-1} + u_2 a_{n-2} + u_3 a_{n-3} = 0,\end{aligned} \tag{154}$$

where $h = r_2$.

The parameters s and t may be determined from the value of u_0 and the regularity condition at $r = 0$. The following different cases must be considered:

(i) $u_0 \neq 0$. We may take $t = 0$; equations (154) for $n = 0$ simplify to

$$\begin{aligned}&(s-\sigma|\kappa|)a_0 - u_0 b_0 = 0,\\ &u_0 a_0 + (s+\sigma|\kappa|)b_0 = 0.\end{aligned} \tag{155}$$

Non-trivial solutions ($a_0 \neq 0$, $b_0 \neq 0$) exist only if the determinant vanishes, i.e. $s^2 - \kappa^2 + u_0^2 = 0$. This yields

$$s = \left[\kappa^2 - u_0^2\right]^{1/2} \tag{156}$$

for the regular solutions. Equations (154) with $t = 0$ give the following recurrence relations

$$\begin{aligned}n(2s+n)a_n &= u_0 A_n + (s+n+\sigma|\kappa|)B_n,\\ n(2s+n)b_n &= -(s+n-\sigma|\kappa|)A_n + u_0 B_n,\end{aligned} \tag{157}$$

with

$$\begin{aligned} A_n &= u_1 a_{n-1} + u_2 a_{n-2} + u_3 a_{n-3}, \\ B_n &= (u_1 - 2ch) b_{n-1} + u_2 b_{n-2} + u_3 b_{n-3}. \end{aligned} \tag{158}$$

These relations, complemented with the values

$$a_0 = 1, \qquad b_0 = (s - \sigma|\kappa|)/u_0, \tag{159}$$

suffice to determine the coefficients in series (153).

(ii) $u_0 = 0, \sigma = 1$. We take $s = |\kappa|$ and $t = 1$. With these values, equations (154) yield

$$\begin{aligned} n a_n &= (u_1 - 2ch) b_{n-2} + u_2 b_{n-3} + u_3 b_{n-4}, \\ (2|\kappa| + n + 1)\, b_n &= -u_1 a_n - u_2 a_{n-1} - u_3 a_{n-2}. \end{aligned} \tag{160}$$

To start the series we set

$$a_0 = 1, \qquad b_0 = -u_1 a_0/(2|\kappa| + 1). \tag{161}$$

(iii) $u_0 = 0, \sigma = -1$. We take $s = |\kappa| + 1$ and $t = -1$. From equations (154) it follows that

$$\begin{aligned} (2|\kappa| + n + 1)\, a_n &= (u_1 - 2ch) b_n + u_2 b_{n-1} + u_3 b_{n-2}, \\ n b_n &= -u_1 a_{n-2} - u_2 a_{n-3} - u_3 a_{n-4}. \end{aligned} \tag{162}$$

The series are started with

$$b_0 = 1, \qquad a_0 = (u_1 - 2ch)/(2|\kappa| + 1). \tag{163}$$

The series (153) are summed with convergence criterion (152). The radial functions at r_2 are renormalized so that

$$P(r_2) = 1, \qquad Q(r_2) = \mathcal{Q}(1)/\mathcal{P}(1). \tag{164}$$

The subroutine package `RADIAL` uses the power series method to solve the radial wave equations to a prescribed accuracy that is fixed by the input value of the parameter ϵ (see eqs. (139) and (152)). This parameter determines, to a large extent, the calculation time. A smaller value of ϵ yields more accurate solutions, but the calculation takes a longer computer time.

Values of the radial functions are delivered for the points of a grid specified by the user, which may be different from the grid where the potential function $\mathcal{V}(r)$ is tabulated. These two grids will be referred to as the "user" grid and the "potential" grid, respectively. In fact, `RADIAL` uses a combined grid, which is obtained by merging the user and potential grids. In what follows, the points of this combined grid are denoted as r_i (i =1, ..., NT). We consider that they are sorted in strictly increasing order (i.e. $r_{i+1} - r_i > 0$) and that $r_1 = 0$. For bound states, the value of $r_{\rm NT}$ must be large enough to guarantee that the probability of finding the particle farther than $r_{\rm NT}$

is negligible (this is important for highly excited bound states). An interesting feature of the present solution method is that the accuracy of the computed wave functions is independent of the spacing of the user grid (except for bound states with many nodes, see below).

In principle, the wave function in each interval (r_i, r_{i+1}) is exactly given by the corresponding series expansion. In practice, however, it may be convenient to split this interval into a number of shorter subintervals in order to speed up the convergence of the series. The `RADIAL` routines automatically select subinterval lengths such that convergence is achieved with less than 60 terms. However, only the values of the radial functions $P(r)$ and $Q(r)$ at the user grid points are transferred to the calling program. In the case of the Schrödinger equation, the output function $Q(r)$ is set equal to the derivative of $P(r)$, i.e. $Q(r) \equiv P'(r)$.

Because of the renormalization of the wave function at the second grid point r_2 (see eqs. (143) and (164)), the computed radial wave functions may reach exceedingly large values (with the risk of leading to computer overflows). To prevent this undesirable effect during the calculation, each time the absolute value of $P(r_i)$ exceeds 100, the calculated radial functions are rescaled by dividing them by $|P(r_i)|$ (but the output radial functions are properly normalized). Notice that, since the rescaling factor is positive, the calculated function $P(r)$ remains positive for small r.

5 Bound states. Eigenvalues

Let us now consider the problem of determining the energy ($E < 0$) and radial functions for bound states with specified quantum numbers. Discrete eigenvalues are located in the interval ($\sim E_{\rm inf}, E_{\rm sup}$) given by

$$E_{\rm inf} \simeq \min\left(V(r) + \frac{\ell(\ell+1)}{2r^2}\right), \qquad E_{\rm sup} \equiv \min\left\{V(r_{\rm NT}) + \frac{\ell(\ell+1)}{2r_{\rm NT}^2}, 0\right\}. \tag{165}$$

$E_{\rm inf}$, the minimum value of the effective radial potential, is a rigorous lower limit for the Schrödinger equation while it is only approximate in the case of the Dirac equation (small variations of this limit are allowed during the numerical calculations so that its exact value does not really matter). The upper limit is fixed by numerical requirements rather than by physical reasons.

The solution procedures for the Schrödinger and Dirac radial equations are similar. For a given energy E in the allowed interval (165), the numerical solution is started at $r = 0$ and extended outwards, by using the power series method described in the last section, up to a certain grid point r_m farther than the outer turning point, determined from the condition

$$V(r_i) > E - \frac{\ell(\ell+1)}{2r_i^2} \qquad \text{if } i \geq m. \tag{166}$$

The first step in the solution is to find a value of the energy E for which the outward solution (from 0 to r_m) has the correct number of zeros given by the radial quantum

number $n_r = n-(\ell+1)$, where n is the principal quantum number. This is accomplished by following a bipartition scheme in the interval (165). It is important to note that the number of zeros of $P(r)$ is determined from its values *at the grid points*; as a consequence it is necessary to use dense enough grids to ensure that there is at most a single zero between consecutive grid points (otherwise, the program will probably ask for a denser user grid).

Once a value of the energy giving the correct number of zeros of the outward solution has been determined, we proceed to compute the solution starting from $r_{\rm NT}$ (or from a grid point far enough from the connection point r_m) and extending it inwards to r_m. The inward solution is then renormalized such that $P(r)$ is continuous at the matching point, i.e. $P_{\rm in}(r_m) = P_{\rm out}(r_m)$. Successive corrections ΔE of the eigenvalue are determined from the discontinuity of $P'(r)$ or $Q(r)$ at r_m by using the method described by Mayers (1957). The `RADIAL` routines are able to detect whether a certain bound state with given quantum numbers occurs.

5.1 Schrödinger equation

The inward solution is started by means of the WKB approximation, which is expected to be fairly accurate for $r \to \infty$. The WKB solution of equation (126) in the region $r > r_m$ is given by (Schiff, 1968)

$$P^{(\rm WKB)}(r) = \mu^{-1/2} \exp\left\{-\int_a^r \mu(r')\,{\rm d}r'\right\}, \tag{167}$$

where

$$\mu(r) \equiv \left\{2\,[V(r)-E] + \frac{\ell(\ell+1)}{r^2}\right\}^{1/2} \tag{168}$$

and a is an arbitrary point in the classically forbidden region ($a > r_m$). Approximation (167) yields a closed formula for the ratio $P'(r)/P(r)$ which, after setting $a = r$, reduces to

$$\frac{P'(r)}{P(r)} = -\frac{1}{2}\mu'\mu^{-1} - \mu. \tag{169}$$

The inward solution is started at a point $r_\infty (\gg r_m)$, where we take $P(r_\infty) = 1$ and use (169) to approximate $P'(r_\infty)$, and extended inwards by using the power series method. The point r_∞ is determined as the minimum grid point satisfying the condition

$$r_\infty\, \mu(r_\infty) > 75, \tag{170}$$

which ensures that $P(r_\infty) \ll P(r_m)$. If this last relation holds, the error introduced by the WKB approximation (167) does not propagate towards the connection point, i.e. the inward solution is stable. When $r_{\rm NT}\mu(r_{\rm NT}) < 75$ we take $r_\infty = r_{\rm NT}$. Further than r_∞ we set $P(r) = 0$. Notice that the last grid point $r_{\rm NT}$ should be larger than r_∞ or at least be far enough from r_m so that the error in the inward solution originating from the WKB formula (169) vanishes at the matching point.

The formula for correcting the eigenvalue may be obtained as follows. Consider the Schrödinger equation (126) written in the form

$$P' = Q, \qquad Q' = 2\left[V(r) - E + \frac{\ell(\ell+1)}{2r^2}\right] P, \tag{171}$$

where P and Q are assumed to depend on r *and* E. From (171) it follows that

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[P^2 \frac{\mathrm{d}}{\mathrm{d}E}\left(\frac{Q}{P}\right)\right] = -2P^2, \tag{172}$$

and, integrating this equation over the arbitrary interval $(r_\mathrm{a}, r_\mathrm{b})$, we get

$$\left[P^2 \frac{\mathrm{d}}{\mathrm{d}E}\left(\frac{Q}{P}\right)\right]_{r_\mathrm{a}}^{r_\mathrm{b}} = -2\int_{r_\mathrm{a}}^{r_\mathrm{b}} P^2(r)\,\mathrm{d}r. \tag{173}$$

Now we assume that the inward solution has been renormalized to match the outward one at the connection point, i.e. $P_\mathrm{out}(r_m) = P_\mathrm{in}(r_m) \equiv P(r_m)$ and, moreover, that the entire function $P(r)$ has been normalized to unity. From eq. (173) we have

$$\begin{aligned} 1 = \int_0^\infty P^2(r)\mathrm{d}r &= -\frac{1}{2}\left\{\left[P^2 \frac{\mathrm{d}}{\mathrm{d}E}\left(\frac{Q}{P}\right)\right]_0^{r_m} + \left[P^2 \frac{\mathrm{d}}{\mathrm{d}E}\left(\frac{Q}{P}\right)\right]_{r_m}^{\infty}\right\} \\ &= -\frac{1}{2}P^2(r_m)\frac{\mathrm{d}}{\mathrm{d}E}\left[\frac{Q_\mathrm{out}(r_m) - Q_\mathrm{in}(r_m)}{P(r_m)}\right], \end{aligned} \tag{174}$$

where the last quantity in the square brackets vanishes when E equals the eigenvalue $E_{n\ell}$. Finally, integrating (174) over E on the interval $(E, E_{n\ell} = E + \Delta E)$ we obtain the eigenvalue correction

$$\Delta E = P(r_m)\left[Q_\mathrm{out}(r_m) - Q_\mathrm{in}(r_m)\right]\left\{2\int_0^\infty P^2(r)\,\mathrm{d}r\right\}^{-1}. \tag{175}$$

5.2 Dirac equation

The methods used to start the inward solution and to correct the eigenvalue are analogous to those adopted for the Schrödinger equation. For large enough radii, the potential energy $V(r)$ becomes negligibly small in comparison with $E + 2c^2$, and equations (127) may be combined to yield the following differential equation for the large component P

$$P''(r) - \mu(r)P(r) = 0, \tag{176}$$

where

$$\mu(r) \equiv \left[\frac{E + 2c^2}{c^2}\Big(V(r) - E\Big) + \frac{\ell(\ell+1)}{r^2}\right]^{1/2}. \tag{177}$$

The point r_∞ is determined as in the case of the Schrödinger equation (see eq. (170)). The inward solution is started there by using the first Dirac equation (127) and relation (169) which yield

$$\frac{Q(r)}{P(r)} \simeq -\frac{c}{E + 2c^2}\left(\frac{\kappa}{r} + \frac{P'(r)}{P(r)}\right) = -\frac{c}{E + 2c^2}\left(\frac{\kappa}{r} - \frac{1}{2}\mu'\mu^{-1} - \mu\right). \tag{178}$$

The formula for the eigenvalue correction reads (Mayers, 1957)

$$\Delta E = cP(r_m)\left[Q_{\rm in}(r_m) - Q_{\rm out}(r_m)\right]\left\{\int_0^\infty \left(P^2(r)+Q^2(r)\right)\mathrm{d}r\right\}^{-1}, \qquad (179)$$

and may be obtained by evaluating the quantity on the left-hand side of eq. (172) from equations (127) and following the same steps as for the Schrödinger equation.

6 Free states. Phase shifts

The series expansion method is also applied to compute radial wave functions for free states ($E > 0$). We recall that, for the considered class of potential functions, $\lim_{r\to\infty} \mathcal{V}(r) = Z$, where Z is a constant. Let $r_{\rm c}$ denote the grid point where the asymptotic value of $\mathcal{V}(r)$ is reached, i.e. the smallest grid point such that $|\mathcal{V}(r) - Z| < \epsilon$ for $r > r_{\rm c}$, where ϵ is the accuracy parameter. Notice that the calculated radial functions have a relative uncertainty of the order of ϵ (see eqs. (139) and (152)). Accordingly, we consider that two quantities are numerically equal when their relative difference is less than ϵ.

In the region $r > r_{\rm c}$, the normalized solution of the Schrödinger equation can be expressed as (Schiff, 1968)

$$\begin{aligned} P(r) &= \cos\delta\ F_\ell(\eta, r) + \sin\delta\ G_\ell(\eta, r), \\ Q(r) &= \cos\delta\ F'_\ell(\eta, r) + \sin\delta\ G'_\ell(\eta, r), \end{aligned} \qquad (180)$$

where $Q(r) = P'(r)$ and $F_\ell(\eta, r)$ and $G_\ell(\eta, r)$ are the regular and irregular Schrödinger-Coulomb functions with $Z{=}\lim_{r\to\infty} \mathcal{V}(r)$ (subsection 3.1). The normalized radial Dirac functions $P(r)$ and $Q(r)$ in the outer region ($r > r_{\rm c}$) satisfy

$$\begin{aligned} P(r) &= \cos\delta\ f^{(\rm u)}(r) + \sin\delta\ g^{(\rm u)}(r), \\ Q(r) &= \cos\delta\ f^{(\rm l)}(r) + \sin\delta\ g^{(\rm l)}(r), \end{aligned} \qquad (181)$$

where $f^{(\rm u,l)}(r)$ and $g^{(\rm u,l)}(r)$ stand for the regular and irregular Dirac-Coulomb functions with $Z{=}\lim_{r\to\infty} \mathcal{V}(r)$ (see subsection 3.4).

The asymptotic behaviour of the Coulomb functions is (section 3)

$$\begin{aligned} F(r), f(r) &\sim \sin\left(kr - \ell\frac{\pi}{2} - \eta\ln 2kr + \Delta\right), \\ G(r), g(r) &\sim \cos\left(kr - \ell\frac{\pi}{2} - \eta\ln 2kr + \Delta\right), \end{aligned} \qquad (182)$$

where k is the particle wave number, η is Sommerfeld's parameter and Δ is the corresponding Coulomb phase shift. It then follows that, for large r,

$$P(r) \sim \sin\left(kr - \ell\frac{\pi}{2} - \eta\ln 2kr + \Delta + \delta\right). \qquad (183)$$

Schrödinger- and Dirac-Coulomb functions are calculated by subroutines `FCOUL` and `DCOUL` described above, which also give an estimate of the relative error of the delivered function values. The magnitude of this error is of the order of 10^{-15} for r larger than the Coulomb turning point, $r_{\rm TP}[0]$. For r less than this value, the accuracy of the calculated Coulomb functions worsens with decreasing r. When $|Z| > \epsilon$, we assume that for the outer grid points the errors in the calculated Coulomb functions are less than the tolerance ϵ (otherwise, the program asks for an extended grid). This implies that, for r-values larger than a certain grid point r_m the radial functions $P(r)$ and $Q(r)$ can be calculated analytically from the expressions (180) and (181).

When $|Z| = 0$ (or, numerically, $< \epsilon$), the Schrödinger- and Dirac-Coulomb functions reduce to spherical Bessel and Neumann functions of integer order, which are accurately given by the function subprogram `BESJN` for any value of r and E. In this case, we set $r_m = r_{\rm c}$ and the radial functions for $r > r_{\rm c}$ are evaluated by using eqs. (180) and (181).

For both the Schrödinger and the Dirac equations, the numerical solution of the radial equation is started at $r = 0$ and extended outwards up to the matching point r_m by using the power series method described in section 4. Let $\overline{P}(r_i)$ and $\overline{Q}(r_i)$ (i=1,...,m) denote the resulting unnormalized radial functions. The normalized solution is obtained by matching the inner numerical function and the outer analytical function at r_m. Notice that, owing to difficulties in computing the Coulomb functions for distances r less than the turning point $r_{\rm TP}[0]$, it may be necessary to extend the inner numerical solution up to values of r that, in the case of low energies and repulsive fields, may be quite large (and this can lengthen the calculation considerably). Of course, for completely screened Coulomb fields ($Z = 0$), the inner solution can be stopped as soon as $|\mathcal{V}(r)| < \epsilon$.

The inner and outer functions are matched by requiring continuity of the $P(r)$ function and its derivative,

$$\begin{aligned} A\,\overline{P}(r_m) &= \cos\delta\; F(r_m) + \sin\delta\; G(r_m), \\ A\,\overline{P}'(r_m) &= \cos\delta\; F'(r_m) + \sin\delta\; G'(r_m), \end{aligned} \tag{184}$$

where F and G stand for the corresponding regular and irregular Coulomb functions. Notice that

$$\begin{aligned} P'(r) &= Q(r) && \text{(Schrödinger)}, \\ P'(r) &= -\frac{\kappa}{r}\,P - \frac{E - V + 2c^2}{c}\,Q(r) && \text{(Dirac)}. \end{aligned} \tag{185}$$

From (184) we obtain (by supressing the argument r_m)

$$\rho \equiv \frac{\overline{P}'}{\overline{P}} = \frac{F' + \tan\delta\; G'}{F + \tan\delta\; G} \tag{186}$$

and

$$\delta = \tan^{-1}\left(\frac{\rho\; F - F'}{G' - \rho\; G}\right), \qquad A = \frac{\cos\delta\; F + \sin\delta\; G}{\overline{P}}. \tag{187}$$

If $|\overline{P}| < \epsilon$, division by $\overline{P}$ is avoided by using the following alternative formulae

$$\delta = \tan^{-1}\left(\frac{-F}{G}\right), \qquad A = \frac{\cos\delta\; F' + \sin\delta\; G'}{\overline{P}'}. \tag{187$'$}$$

The normalized inner function is

$$P(r_i) = A\,\overline{P}(r_i), \quad Q(r_i) = A\,\overline{Q}(r_i) \quad (i = 1, \ldots, m). \tag{188}$$

In order to fix the global sign of the radial function, we require $P(r)$ to be positive for small r and, consequently, we use the branch of the multivalued $\tan^{-1}$ function that makes the inner normalization constant, A, positive.

The "inner" phase shift δ is only due to the short-range distortion of the asymptotic Coulomb field, $\mathcal{V}_{\rm sr}(r) \equiv \mathcal{V}(r) - Z$; the effect of the Coulomb field is accounted for by the logarithmic phase, $-\eta \ln 2kr$, and the Coulomb phase shift Δ. For a pure Coulomb field ($\mathcal{V}_{\rm sr} \equiv 0$), $\delta = 0$. Attractive (repulsive) short-range fields give positive (negative) inner phase shifts. These phase shifts are indeterminate in a multiple of 2π. Notice that if it were not for the fact that $P(r)$ is required to be positive for small r, the inner phase shifts would be indeterminate in a multiple of π. We shall always reduce the calculated values of δ to the interval $(-\pi,\pi)$ so as to get rid of this indeterminacy when $|\delta| < \pi$.

7 Structure of the RADIAL subroutines

All the real variables are handled in double precision. The input of the solution subroutines contains the parameter EPS ($= \epsilon$, cf. eqs. (139) and (152)) which controls the global accuracy of the numerical procedure; the relative numerical uncertainty in the results is of the order of 100×EPS. Calculation time increases when EPS is reduced. With double-precision arithmetic, optimum accuracy is obtained with EPS$\simeq 10^{-15}$. We recall that all quantities are in generalized atomic units.

The subroutines to be called from the MAIN program are the following:

1) SUBROUTINE VINT(R,RV,NV).
This is an initialization routine which determines the cubic spline that interpolates the potential function. The values of the potential function $\mathcal{V}(r_i) = r_i V(r_i)$ at the grid points r_i ($i = 1, \ldots,$ NV) are entered as the first NV components of the arrays RV and R respectively, which are kept unaltered. The dimension of these arrays is NDIM (see below). The r values must be given in increasing order with R(1)=0.0D0. A pair of repeated r values is interpreted as a discontinuity of the potential (or its derivatives).

2) SUBROUTINE SBOUND(E,EPS,DELL,N,L).
Determination of Schrödinger bound-state radial functions and eigenvalues.

INPUT: E = estimated eigenvalue (a good estimate speeds up the calculation but it is not essential).
DELL = eigenvalue tolerance (i.e. maximum acceptable relative error in E).
N = principal quantum number n. L = ℓ.

OUTPUT: E = eigenvalue.
Radial functions $P(r)$ and $Q(r) \equiv P'(r)$ (see below).

3) `SUBROUTINE SFREE(E,EPS,PHASE,L)`.
Calculation of Schrödinger free-state radial functions and phase shifts.

INPUT: `E` = kinetic energy. `L` = ℓ.
OUTPUT: `PHASE` = inner phase shift δ (in radians).
Radial functions $P(r)$ and $Q(r) \equiv P'(r)$ (see below).

4) `SUBROUTINE DBOUND(E,EPS,DELL,N,K)`.
Determination of Dirac bound-state radial functions and eigenvalues.

INPUT: `E` = estimated eigenvalue. `DELL` = eigenvalue tolerance.
`N` = principal quantum number n. `K` = κ.
OUTPUT: `E` = eigenvalue.
Radial functions $P(r)$ and $Q(r)$ (see below).

5) `SUBROUTINE DFREE(E,EPS,PHASE,K)`.
Calculation of Dirac free-state radial functions and phase shifts.

INPUT: `E` = kinetic energy. `K` = κ.
OUTPUT: `PHASE` = inner phase shift δ (in radians).
Radial functions $P(r)$ and $Q(r)$ (see below).

The values of the radial functions at the points r_i ($i = 1, \ldots,$ `NGP`) of a grid arbitrarily selected by the user (which may be different from the grid where the potential function is tabulated) are delivered through the named common block

```
COMMON/RADWF/RAD(NDIM),P(NDIM),Q(NDIM),NGP,ILAST,IER
```

The array `RAD` contains the input grid points r_i ($i = 1, \ldots,$ `NGP`) in the first `NGP` positions. At the output, the arrays `P` and `Q` contain the values of P(`RAD(I)`) and Q(`RAD(I)`) stored in their `I`-th positions ($Q \equiv P'$ for the Schrödinger equation). The dimension of the arrays is `NDIM` (see below). For bound states, `ILAST` is the index corresponding to the practical infinity, i.e. `RAD(ILAST)`$= r_\infty$. For free states, `ILAST` is the index of the matching point, `RAD(ILAST)`$= r_m$. Bound-state radial functions are normalized to unity; the normalization is carried out by interpolating the radial functions with natural cubic splines and integrating the squared splines. If the spacing between the grid points is not small enough, the normalization may be in serious error, i.e. the given radial functions may differ from the exact solution by a constant factor. Free-state radial functions are normalized to asymptotic unit amplitude. Notice that the calculated radial function $P(r)$ is positive for small r.

The value of `NDIM`, which defines the array dimensions, is set as a parameter in the source listing and must be the same in all subroutines and in the `MAIN` program (since otherwise the variables in the common blocks would not be correctly aligned). In the original `RADIAL` code, it is set to 800. This value must be changed by the user, by editing the source files, when a larger number of grid points is required.

The variable `IER` in the common block `RADWF` is an error indicator: its output value is zero when the calculation has been successfully ended, a positive value is returned when some fatal error is found during the calculation (in this case an error message is also written in the output file). The output value of `IER` indicates the type of detected

error. A list of error codes and tentative solutions is given in the source listing. The program stops when an obvious inconsistency in the input data is detected.

In the case of free states, the radial functions for $r >$`RAD(NGP)` can be obtained analytically from eqs. (180) and (181), with the help of subroutines `SCOUL` and `DCOUL` (which compute Schrödinger- and Dirac-Coulomb functions, respectively). For fields such that $\lim_{r\to\infty} \mathcal{V}(r) = 0$, the radial functions for $r >$`RAD(NGP)` should be calculated in terms of the spherical Bessel functions of integer order (which are computed by function `BESJN`). At output, the common block

```
COMMON/OCOUL/WAVENUM,ETA,DELTA
```

contains the values of the wave number, k (=`WAVENUM`), the Sommerfeld parameter, η (=`ETA`), and the Coulomb phase shift, Δ (=`DELTA`) in radians. With these values available, the calculation of Coulomb functions for large r's can be substantially simplified by using the asymptotic expansion given by eqs. (71) and (75).

Although `RADIAL` has been devised to handle fields such that $V(r)$ goes to zero at large distances, it can also be used to compute bound states for potentials that diverge at $r = \infty$ (e.g. the isotropic harmonic oscillator potential, $V(r) \propto r^2$). For these fields, we can start from a table of values of $V(r)$ for a certain grid r_i $(i = 1, \ldots, \mathrm{NT})$, suitably spaced to minimize spline interpolation errors, and define the shifted potential function $\mathcal{V}(r) \equiv r[V(r) - V(r_{\mathrm{NT}})]$, which vanishes at the outer grid point. This point must be selected such that, for the considered bound state, the probability of having the particle farther than r_{NT} is negligible. It is important to meet this condition, since `RADIAL` sets $\mathcal{V}(r) = \mathcal{V}(r_{\mathrm{NT}})$ for $r > R_{\mathrm{NT}}$. With the shifted potential, `RADIAL` then gives the desired bound-state radial functions; the output value of the energy is $E - V(r_{\mathrm{NT}})$, where E is the eigenenergy for the actual field $V(r)$.

8 Test program

The `RADIAL` package is accompanied with a simple `MAIN` program called `DEMORAD` that calculates bound- and free-state radial functions for partially screened Coulomb fields of the form

$$V(r) = \frac{Z}{r} + \frac{Z_{\mathrm{S}}}{r} \exp(-Ar). \tag{189}$$

With properly selected parameters, this potential may be used to approximate the interactions that occur in atomic physics (atomic structure, photoionization, collisions of charged particles with atoms and ions, ...). The program `DEMORAD` can be run interactively and the input/output is self-explanatory. Radial functions are written in the output file `WAVES.DAT`, in a format ready to be imported by a plotting program for visualization. Examples of results produced by `DEMORAD` are given below, in the test run output.

The user and potential grids, r_i $(i = 1, \ldots, N)$, adopted in the `DEMORAD` program are identical and defined as

$$r_1 = 0 \quad \text{and} \quad \mathcal{G}(r_i) \equiv a\, r_i + b \ln r_i + c = i \quad (i = 2, \ldots, N), \tag{190}$$

with

$$a = 1/\texttt{STEP}, \quad b = 1/\ln(\texttt{RATIO}), \quad c = N - ar_N - b\ln r_N. \tag{191}$$

The quantities STEP, RATIO, and r_N are parameters, which are appropriately selected. With RATIO$\ll$1, we get a nearly uniform grid with spacing $r_i - r_{i-1} \simeq$ STEP. Taking STEP=0, we obtain a logarithmic grid such that $r_i/r_{i-1} =$ RATIO. With a value of RATIO slightly larger than unity, say RATIO=1.15, a number of points, N, of the order of 600 or larger and $r_N \simeq (N - 100)$STEP, the grid is nearly logarithmic in the vicinity of $r = 0$ and nearly uniform at large r. In this case we get a high density of points near the origin (which is convenient in order to have a good representation of bound states) and a nearly uniform grid at large distances from the origin (as required to follow the regular oscillations of free-state wave functions in the asymptotic region). Notice that, for free states, a value of STEP of the order of 0.05 times the wavelength λ $(= 2\pi/k)$ automatically locates at least 20 points within a wavelength. This kind of grid is also very convenient for further numerical calculations. Thus, to evaluate integrals involving radial functions, we simply change to the new variable $i = \mathcal{G}(r)$ to get the integrand tabulated in a uniform grid, with unit spacing, so that the integral can be routinely calculated e.g. by Simpson's method. Interpolation from the uniform i-grid is also easier than in the r-grid. Notice, however, that the first interval (r_1, r_2) must be considered separately. The subroutine GRID, included in the source file DEMORAD.FOR, generates the grid (190) for the selected parameters. The grids used in DEMORAD are such that the output radial functions usually look smooth when plotted using straight segments to join the data points.

RADIAL provides radial functions, eigenvalues and phase shifts *for the potential function given by the cubic spline* (128). Calculation results are affected by numerical uncertainties that arise not only from round-off errors (which can be reduced by using a smaller accuracy parameter ϵ) but also from differences between the spline aproximation and the actual potential function $\mathcal{V}(r)$. In general, we shall deal with potentials that are either given in analytical form or defined numerically by means of a table $\mathcal{V}(r_i)$ $(i = 1, \ldots, N)$. For analytical potentials, we can always determine a radial grid r_i that is dense enough to make sure that the corresponding natural cubic spline differs from the actual potential function by less than a selected tolerance. Thus, for the analytical fields (189) and the grids used in DEMORAD, the relative error introduced by the spline interpolation is less than 10^{-6}. In a few particular cases (namely, piecewise Coulomb, constant, linear or quadratic fields) the spline interpolation is exact, irrespective of the number of grid points, and the calculated results are only affected by round-off errors.

When the potential function $\mathcal{V}(r)$ is given in numerical form, the error introduced by the spline approximation may be difficult to estimate. As mentioned in the introduction, one must at least make sure that the interpolating spline does not wiggle between the tabulated data; this may happen when the potential grid points are spaced too far apart. To get an idea of the magnitude of the interpolation error in the vicinity of the grid point r_k, we can consider the natural cubic spline that interpolates the potential table with the k-th point removed. The difference between the value of this spline at r_k and the datum $\mathcal{V}(r_k)$ then gives the sought error estimate. The subroutine ERRSPL, which is included in the source code DEMORAD.FOR, uses this method to determine the maximum

relative error introduced by natural cubic spline interpolation in a given table. This subroutine may be helpful to check whether a given radial grid is adequately spaced to permit spline interpolation of $\mathcal{V}(r)$ to the required accuracy.

Test run output

```
****  SCHRODINGER EQ. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      BOUND STATE: N=   1, L=   0   (EPS= 1.0E-13)
      BINDING ENERGY =-1.067816660378799E+03

****  DIRAC EQUATION. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      BOUND STATE: N=   1, K=  -1   (EPS= 1.0E-13)
      BINDING ENERGY =-1.115472538267358E+03

****  SCHRODINGER EQ. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      BOUND STATE: N=  10, L=   5   (EPS= 1.0E-13)
      BINDING ENERGY =-5.000000000005560E-03

****  DIRAC EQUATION. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      BOUND STATE: N=  10, K=   5   (EPS= 1.0E-13)
      BINDING ENERGY =-5.000003328218895E-03

****  SCHRODINGER EQ. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      FREE STATE: E= 1.000000E+02, L=   0   (EPS= 1.0E-13)
        INNER PHASE SHIFT=-8.870875130050138E-01
      COULOMB PHASE SHIFT= 4.067401266229027E-02   (ETA=-7.071068E-02)

****  DIRAC EQUATION. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      FREE STATE: E= 1.000000E+02, K=  -1   (EPS= 1.0E-13)
        INNER PHASE SHIFT=-7.124212735575739E-01
      COULOMB PHASE SHIFT= 4.069204642944557E-02   (ETA=-7.099277E-02)

****  SCHRODINGER EQ. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      FREE STATE: E= 1.000000E+02, L=   5   (EPS= 1.0E-13)
        INNER PHASE SHIFT= 5.109874444042619E-01
      COULOMB PHASE SHIFT=-1.206426693445105E-01   (ETA=-7.071068E-02)

****  DIRAC EQUATION. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      FREE STATE: E= 1.000000E+02, K=   5   (EPS= 1.0E-13)
        INNER PHASE SHIFT= 5.165575947733907E-01
      COULOMB PHASE SHIFT=-1.210779425766962E-01   (ETA=-7.099277E-02)

****  DIRAC EQUATION. POTENTIAL FUNCTION: R*V(R)=Z+ZS*DEXP(-A*R)
      Z=-1.000000E+00, ZS =-5.000000E+01, A= 5.000000E+00
      FREE STATE: E= 1.000000E+02, K=  10   (EPS= 1.0E-13)
        INNER PHASE SHIFT= 5.837929241068245E-02
      COULOMB PHASE SHIFT=-1.669349756666961E-01   (ETA=-7.099277E-02)
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Appendix A. Cubic spline interpolation

In this appendix we follow the presentation of Maron (1982). Suppose that a function $f(x)$ is given in numerical form, i.e. as a table of values

$$f_i = f(x_i) \qquad (i = 1, \ldots, N). \tag{A.1}$$

The points (knots) x_i do not need to be equispaced, but we assume that they are in (strictly) increasing order

$$x_1 < x_2 < \cdots < x_N. \tag{A.2}$$

A function $\varphi(x)$ is said to be an interpolating cubic spline if

1) It reduces to a cubic polynomial within each interval $[x_i,x_{i+1}]$, i.e. if $x_i \le x \le x_{i+1}$

$$\varphi(x) = a_i + b_i x + c_i x^2 + d_i x^3 \equiv p_i(x) \qquad (i = 1, \ldots, N-1). \tag{A.3}$$

2) The polynomial $p_i(x)$ matches the values of $f(x)$ at the end-points of the i-th interval,

$$p_i(x_i) = f_i, \quad p_i(x_{i+1}) = f_{i+1} \qquad (i = 1, \ldots, N-1), \tag{A.4}$$

so that $\varphi(x)$ is continuous in $[x_1,x_N]$.

3) The first and second derivatives of $\varphi(x)$ are continuous in $[x_1,x_N]$

$$p_i'(x_{i+1}) = p_{i+1}'(x_{i+1}) \qquad (i = 1, \ldots, N-2), \tag{A.5}$$

$$p_i''(x_{i+1}) = p_{i+1}''(x_{i+1}) \qquad (i = 1, \ldots, N-2). \tag{A.6}$$

Consequently, the curve $y = \varphi(x)$ interpolates the table (A.1) and has a continuously turning tangent.

To obtain the spline coefficients a_i, b_i, c_i, d_i $(i = 1, \ldots, N-1)$ we start from the fact that $\varphi''(x)$ is linear in $[x_i,x_{i+1}]$. Introducing the quantities

$$h_i \equiv x_{i+1} - x_i \qquad (i = 1, \ldots, N-1) \tag{A.7}$$

and

$$\sigma_i = \varphi''(x_i) \qquad (i = 1, \ldots, N), \tag{A.8}$$

we can write the obvious identity

$$p_i''(x) = \sigma_i \frac{x_{i+1} - x}{h_i} + \sigma_{i+1} \frac{x - x_i}{h_i} \qquad (i = 1, \ldots, N-1). \tag{A.9}$$

Notice that x_{i+1} must be larger than x_i in order to have $h_i > 0$. Integrating eq. (A.9) twice with respect to x gives for $i = 1, \ldots, N-1$

$$p_i(x) = \sigma_i \frac{(x_{i+1} - x)^3}{6h_i} + \sigma_{i+1} \frac{(x - x_i)^3}{6h_i} + A_i(x - x_i) + B_i(x_{i+1} - x), \tag{A.10}$$

where A_i and B_i are constants. These can be determined by introducing the expression (A.10) into eqs. (A.4); this gives the pair of eqs.

$$\sigma_i \frac{h_i^2}{6} + B_i h_i = f_i \qquad \text{and} \qquad \sigma_{i+1} \frac{h_i^2}{6} + A_i h_i = f_{i+1}. \tag{A.11}$$

Finally, solving for A_i and B_i and substituting the result in (A.10), we obtain

$$\begin{aligned} p_i(x) &= \frac{\sigma_i}{6}\left[\frac{(x_{i+1}-x)^3}{h_i} - h_i(x_{i+1}-x)\right] + f_i\frac{x_{i+1}-x}{h_i} \\ &\quad + \frac{\sigma_{i+1}}{6}\left[\frac{(x-x_i)^3}{h_i} - h_i(x-x_i)\right] + f_{i+1}\frac{x-x_i}{h_i}. \end{aligned} \tag{A.12}$$

To be able to use $\varphi(x)$ to approximate $f(x)$, we must find the second derivatives σ_i $(i = 1, \ldots, N)$. To this end, we impose the conditions (A.5). Differentiating (A.12) gives

$$p_i'(x) = \frac{\sigma_i}{6}\left[-\frac{3(x_{i+1}-x)^2}{h_i} + h_i\right] + \frac{\sigma_{i+1}}{6}\left[\frac{3(x-x_i)^2}{h_i} - h_i\right] + \delta_i, \tag{A.13}$$

where

$$\delta_i = \frac{y_{i+1}-y_i}{h_i}. \tag{A.14}$$

Hence,

$$p_i'(x_{i+1}) = \sigma_i\frac{h_i}{6} + \sigma_{i+1}\frac{h_i}{3} + \delta_i, \tag{A.15a}$$

$$p_i'(x_i) = -\sigma_i\frac{h_i}{3} - \sigma_{i+1}\frac{h_i}{6} + \delta_i, \tag{A.15b}$$

and, similarly,

$$p_{i+1}'(x_{i+1}) = -\sigma_{i+1}\frac{h_{i+1}}{3} - \sigma_{i+2}\frac{h_{i+1}}{6} + \delta_{i+1}. \tag{A.15c}$$

Replacing (A.15a) and (A.15c) in (A.5), we obtain

$$h_i\sigma_i + 2(h_i + h_{i+1})\sigma_{i+1} + h_{i+1}\sigma_{i+2} = 6\,(\delta_{i+1} - \delta_i) \qquad (i = 1, \ldots, N-2). \tag{A.16}$$

The system (A.16) is linear in the N unknowns σ_i $(i = 1, \ldots, N)$. However, since it contains only $N-2$ equations, it is underdetermined. This means that we need either to add two additional (independent) equations or to fix arbitrarily two of the N unknowns. The usual practice is to adopt *endpoint strategies* that introduce constraints on the behaviour of $\varphi(x)$ near x_1 and x_N. An endpoint strategy fixes the values of σ_1 and σ_N, yielding an $(N-2)\times(N-2)$ system in the variables σ_i $(i = 2, \ldots, N-1)$. The resulting system is, in matrix form,

$$\begin{pmatrix} H_2 & h_2 & 0 & \cdots & 0 & 0 & 0 \\ h_2 & H_3 & h_3 & \cdots & 0 & 0 & 0 \\ 0 & h_3 & H_4 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & H_{N-3} & h_{N-3} & 0 \\ 0 & 0 & 0 & \cdots & h_{N-3} & H_{N-2} & h_{N-2} \\ 0 & 0 & 0 & \cdots & 0 & h_{N-2} & H_{N-1} \end{pmatrix} \begin{pmatrix} \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \vdots \\ \sigma_{N-3} \\ \sigma_{N-2} \\ \sigma_{N-1} \end{pmatrix} = \begin{pmatrix} D_2 \\ D_3 \\ D_4 \\ \vdots \\ D_{N-3} \\ D_{N-2} \\ D_{N-1} \end{pmatrix}, \tag{A.17}$$

where

$$H_i = 2(h_{i-1} + h_i) \qquad (i = 2, \ldots, N-1) \tag{A.18}$$

and

$$\begin{aligned} D_2 &= 6(\delta_2 - \delta_1) - h_1\sigma_1, \\ D_i &= 6(\delta_i - \delta_{i-1}) \qquad\qquad (i = 3, \ldots, N-2), \\ D_{N-1} &= 6(\delta_{N-1} - \delta_{N-2}) - h_{N-1}\sigma_N. \end{aligned} \tag{A.19}$$

(σ_1 and σ_N are removed from the first and last equations, respectively). The matrix of coefficients is symmetric, tridiagonal and diagonally dominant (the larger coefficients are in the diagonal), so that the system (A.17) can be easily (and accurately) solved by Gauss elimination. The spline coefficients a_i, b_i, c_i, d_i ($i = 1, \ldots, N-1$) –see eq. (A.3)– can then be obtained by expanding the expressions (A.12):

$$\begin{aligned} a_i &= \frac{1}{6h_i}\left[\sigma_i x_{i+1}^3 - \sigma_{i+1}x_i^3 + 6\left(f_i x_{i+1} - f_{i+1}x_i\right)\right] + \frac{h_i}{6}\left(\sigma_{i+1}x_i - \sigma_i x_{i+1}\right), \\ b_i &= \frac{1}{2h_i}\left[\sigma_{i+1}x_i^2 - \sigma_i x_{i+1}^2 + 2\left(f_{i+1} - f_i\right)\right] + \frac{h_i}{6}\left(\sigma_i - \sigma_{i+1}\right), \\ c_i &= \frac{1}{2h_i}\left(\sigma_i x_{i+1} - \sigma_{i+1}x_i\right), \\ d_i &= \frac{1}{6h_i}\left(\sigma_{i+1} - \sigma_i\right). \end{aligned} \tag{A.20}$$

When accurate values of $f''(x)$ are known, the best strategy is to set $\sigma_1 = f''(x_1)$ and $\sigma_N = f''(x_N)$, since this will minimize the spline interpolation errors. Unfortunately, the exact values $f''(x_1)$ and $f''(x_N)$ are not always available.

The so-called *natural spline* corresponds to taking $\sigma_1 = \sigma_N = 0$. It results in a $y = \varphi(x)$ curve with the shape that would be taken by a flexible rod (such as a draughtsman's spline) if it were bent around pegs at the knots but allowed to maintain its natural (straight) shape outside the interval $[x_1,x_N]$. Since $\sigma_1 = \sigma_N = 0$, extrapolation of $\varphi(x)$ outside the interval $[x_1,x_N]$ by straight segments gives a continuous function with continuous first and second derivatives (i.e. a cubic spline in $[-\infty,\infty]$).

The accuracy of the spline interpolation is mainly determined by the density of knots in the regions where $f(x)$ has strong variations. For constant, linear, quadratic and cubic functions the interpolation errors can be reduced to zero by using the exact values of σ_1 and σ_N (in these cases, however, the natural spline may introduce appreciable errors near the endpoints). It is important to keep in mind that a cubic polynomial has, at most, one inflexion point. As a consequence, we should have at least a knot between each pair of inflexion points of $f(x)$ to ensure proper interpolation. Special care must be taken when interpolating functions that have a practically constant value in a partial interval, since the spline tends to wiggle instead of staying constant. In this particular case, it may be more convenient to use linear interpolation.

Obviously, the interpolating cubic spline $\varphi(x)$ can be used not only to obtain inter-

polated values of $f(x)$ between the knots, but also to calculate integrals such as

$$\int_a^b f(x)\,\mathrm{d}x \simeq \int_a^b \varphi(x)\,\mathrm{d}x, \qquad x_1 \le a \ \text{ and } \ b \le x_N, \tag{A.21}$$

analytically. It is worth noting that derivatives of $\varphi(x)$ other than the first one may differ significantly from those of $f(x)$.

To obtain the interpolated value $\varphi(x_\mathrm{c})$ −see eq. (A.3)− of $f(x)$ at the point x_c, we must first determine the interval $[x_i,x_{i+1}]$ that contains the point x_c. To reduce the effort to locate the point, we use the following binary search algorithm

(i) Set i =1 and $j = N$.

(ii) Set $k = [(i + j)/2]$.

(iii) If $x_k < x_\mathrm{c}$, set $i = k$; otherwise set $j = k$.

(iv) If $j - i > 1$, go to step (ii).

(v) Deliver i.

Notice that the maximum delivered value of i is $N - 1$.

Appendix B. Continued fractions

Continued fractions are often useful to evaluate special functions (see Press et al., 1992). A continued fraction is defined as

$$f(x) = b_0 + \cfrac{a_1}{b_1 + \cfrac{a_2}{b_2 + \cfrac{a_3}{b_3 + \cdots}}}, \tag{B.1}$$

where the a's and b's can themselves be simple functions of x. The continued fraction (B.1) is frequently written in the typographically simpler form

$$f(x) = b_0 + \frac{a_1}{b_1+}\,\frac{a_2}{b_2+}\,\frac{a_3}{b_3 + \cdots}. \tag{B.2}$$

If the number of terms is finite, f is called a terminating continued fraction. If the number of terms is infinite, f is called an infinite continued fraction and the terminating fraction

$$f_n(x) = b_0 + \frac{a_1}{b_1+}\,\frac{a_2}{b_2+} \cdots \frac{a_n}{b_n} \tag{B.3}$$

is called the n-th convergent of f. If $\lim_{n\to\infty} f_n(x)$ exists, the infinite continued fraction $f(x)$ is said to be convergent, and the limit is then the value of the continued fraction. Continued fractions frequently converge much more rapidly than power series expansions and in a wider domain of the complex plane.

In the calculation of terminating continued fractions, is seems natural to proceed from right to left. But this is not an efficient method to compute infinite fractions. It is much more effective to proceed from left to right by using the following recursion method, which was invented by Wallis a long while ago (in 1655!). Let us define two sequences, A_n and B_n, by the initial values

$$A_{-1} = 1, \quad A_0 = b_0, \quad B_{-1} = 0, \quad B_0 = 1 \tag{B.4a}$$

and the recurrence relations

$$A_n = A_{n-1}b_n + A_{n-2}a_n, \qquad B_n = B_{n-1}b_n + B_{n-2}a_n; \tag{B.4b}$$

then, the n-th convergent of f is

$$f_n(x) = \frac{A_n}{B_n}. \tag{B.5}$$

This result can be easily proved by induction. The recurrence (B.4) frequently generates very large or very small values of the partial numerators and denominators A_n and B_n, with the risk of overflow or underflow of the floating point representation. However, as the recurrence (B.4) is linear, this can be fixed by simply rescaling the values A_n, A_{n-1}, B_n and B_{n-1}, for instance dividing all them by $|B_n|$, when an overflow is imminent[4]. A brute force solution, easier to program, is to rescale after each iteration. If one of the denominators B_n equals 0 (as it may happen in the case of Coulomb functions), we must skip the rescaling and evaluation of the ratio (B.5) and continue with the next iteration of (B.4); a second zero could indicate that the continued fraction is not convergent. We assume that the numerical evaluation of the continued fraction can be terminated when the values $f_n(x)$ and $f_{n-1}(x)$ of the last iterations differ in less than the selected tolerance. This is normally a good termination method (it certainly works for Coulomb functions), although it may yield wrong results with peculiar fractions (such that $f_{n-1} = f_n$ but $f_{n+1} \neq f_n$). More sofisticated algorithms for evaluating continued fractions, which avoid the need for rescaling intermediate results, have been proposed by Steed (Barnett et al., 1974) and by Lentz (see Press et al., 1992).

The equivalence transformation

$$a_k \to ca_k, \quad b_k \to cb_k, \quad a_{k+1} \to ca_{k+1}, \tag{B.6}$$

with $c \neq 0$, keeps the value of the continued fraction unchanged. Successive equivalence transformations with different c's can be applied to successive terms to simplify the form of the a and b coefficients:

$$f(x) = b_0 + \frac{c_1 a_1}{c_1 b_1 +} \, \frac{c_1 c_2 a_2}{c_2 b_2 +} \cdots \frac{c_{n-1} c_n a_n}{c_n b_n + \cdots}. \tag{B.7}$$

[4]The use of a positive scaling factor is important so as to keep track of the true sign of the partial denominator, which is required to determine the sign of the Coulomb functions computed by Steed's continued fraction method.

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