Chapter 1
Potential Scattering

In this chapter we introduce the basic concepts of atomic collision theory by considering potential scattering. While being of interest in its own right, this chapter also provides a basis for our treatment of electron and positron collisions with atoms, ions and molecules in later chapters in this monograph. We commence in Sect. 1.1 by considering the solution of the non-relativistic time-independent Schrödinger equation for a short-range spherically symmetric potential. This enables us to define the scattering amplitude and various cross sections and to obtain explicit expressions for these quantities in terms of the partial wave phase shifts. We also introduce and define the K-matrix, S-matrix and T-matrix in terms of the partial wave phase shifts and we obtain an integral expression for the K-matrix and the phase shift. In Sect. 1.2 we extend this discussion to consider the situation where a long-range Coulomb potential is present in addition to a short-range potential. We obtain expressions for the scattering amplitude and the differential cross section for pure Coulomb scattering and where both a Coulomb potential and a short-range potential are present. In Sect. 1.3 we turn our attention to the analytic properties of the partial wave S-matrix in the complex momentum plane and we discuss the connection between poles in the S-matrix and bound states and resonances. In Sect. 1.4 we extend this discussion of analytic properties to consider the analytic behaviour of the phase shift and the scattering amplitude in the neighbourhood of threshold energy both for short-range potentials and for potentials behaving asymptotically as r^{-s} where $s \geq 2$. Also in this section, we consider the threshold behaviour when a Coulomb potential is present in addition to a short-range potential, corresponding to electron scattering by a positive or negative ion. Next in Sect. 1.5 we derive variational principles first obtained by Kohn for the partial wave phase shift and for the S-matrix. We conclude this chapter by considering in Sect. 1.6 relativistic scattering of an electron by a spherically symmetric potential. This situation occurs for relativistic electron scattering energies or when an electron is scattered by heavy atoms or ions. In this case the time-independent Dirac equation, which takes into account both the spin and the relativistic behaviour of the scattered electron must be solved. Finally we note that some of these topics have been discussed in greater detail in monographs devoted to potential scattering by Burke [158] and Burke and Joachain [171].

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1.1 Scattering by a Short-Range Potential

We initiate our discussion of potential scattering by considering the solution of the non-relativistic time-independent Schrödinger equation describing the motion of a particle of unit mass in a potential $V(\mathbf{r})$. We write this equation in atomic units as

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})\,, \tag{1.1}$$

where E is the total energy and $\psi(\mathbf{r})$ is the wave function describing the motion of the scattered particle. We assume in this section that the potential $V(\mathbf{r})$ is short range, vanishing faster than r^{-1} at large distances. We also assume that the potential is less singular than r^{-2} at the origin.

The solution of (1.1), corresponding to the particle incident on the scattering centre in the z-direction and scattered in the direction $\Omega \equiv (\theta, \phi)$ defined by the polar angles θ and ϕ, has the asymptotic form

$$\psi(\mathbf{r}) \underset{r\to\infty}{\sim} \mathrm{e}^{\mathrm{i}kz} + f(\theta,\phi)\frac{\mathrm{e}^{\mathrm{i}kr}}{r}\,, \tag{1.2}$$

where $f(\theta, \phi)$ is the scattering amplitude and the wave number k of the scattered particle is related to the total energy E by

$$k^2 = 2E\,. \tag{1.3}$$

If the potential behaves as r^{-1} at large distances, corresponding to a long-range Coulomb potential, then logarithmic phase factors must be included in the exponentials in (1.2) to allow for the distortion caused by the Coulomb potential. We consider this possibility in Sect. 1.2.

The differential cross section can be obtained from (1.2) by calculating the outward flux of particles scattered through a spherical surface $r^2\mathrm{d}\Omega$ for large r divided by the incident flux and by the element of solid angle $\mathrm{d}\Omega$. This gives

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta,\phi)|^2\,, \tag{1.4}$$

in units of a_0^2 per steradian. The total cross section is then obtained by integrating the differential cross section over all scattering angles giving

$$\sigma_{\mathrm{tot}} = \int_0^{2\pi}\int_0^{\pi} |f(\theta,\phi)|^2 \sin\theta \mathrm{d}\theta\mathrm{d}\phi\,, \tag{1.5}$$

in units of a_0^2. A further cross section, of importance in the study of the motion of electron swarms in gases, is the momentum transfer cross section defined by

$$\sigma_M = \int_0^{2\pi}\int_0^{\pi} |f(\theta,\phi)|^2 (1-\cos\theta)\sin\theta \mathrm{d}\theta\mathrm{d}\phi\,. \tag{1.6}$$

In order to determine the scattering amplitude it is necessary to solve (1.1) for $\psi(\mathbf{r})$ subject to the asymptotic boundary condition (1.2). For low and intermediate energy scattering this is most conveniently achieved by making a partial wave analysis. This method was originally used in the treatment of scattering of sound waves by Rayleigh [779] and was first applied to the problem of scattering of electrons by atoms by Faxén and Holtsmark [314].

We consider the case of a spherically symmetric "reduced" potential $U(r) = 2V(r)$. We can expand the wave function $\psi(\mathbf{r})$ as

$$\psi(\mathbf{r}) = \sum_{\ell=0}^{\infty} B_\ell(k) r^{-1} u_\ell(r) P_\ell(\cos\theta)\,, \tag{1.7}$$

where ℓ is the orbital angular momentum quantum number of the particle, $P_\ell(\cos\theta)$ are Legendre polynomials defined in Appendix B and the coefficients $B_\ell(k)$ are determined below by requiring that the asymptotic boundary condition (1.2) is satisfied. The equation satisfied by the reduced radial wave function $u_\ell(r)$, which does not include the r^{-1} factor in (1.7), is determined by substituting (1.7) into (1.1), premultiplying by $P_\ell(\cos\theta)$ and integrating with respect to $\cos\theta$. We find that $u_\ell(r)$ satisfies the radial Schrödinger equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2\right) u_\ell(r) = 0\,. \tag{1.8}$$

We note that the effective potential in this equation is the sum of the reduced potential $U(r)$ and the repulsive centrifugal barrier term $\ell(\ell+1)/r^2$. We also remark that since we are considering real potentials $U(r)$, as well as real energies and angular momenta, there is no loss of generality in assuming that $u_\ell(r)$ is real.

We look for a solution of (1.8) satisfying the boundary conditions

$$\begin{aligned} u_\ell(0) &\underset{r\to 0}{\sim} n r^{\ell+1}\,, \\ u_\ell(r) &\underset{r\to\infty}{\sim} s_\ell(kr) + c_\ell(kr)\tan\delta_\ell(k)\,, \end{aligned} \tag{1.9}$$

where n is a normalization factor and $s_\ell(kr)$ and $c_\ell(kr)$ are solutions of (1.8) in the absence of the potential $U(r)$, which are, respectively, regular and irregular at the origin. We show in Appendix C.2 that they can be written for integral values of ℓ in terms of spherical Bessel and Neumann functions $j_\ell(kr)$ and $n_\ell(kr)$ as follows:

$$s_\ell(kr) = kr j_\ell(kr) = \left(\frac{\pi kr}{2}\right)^{\frac{1}{2}} J_{\ell+\frac{1}{2}}(kr) \underset{r\to\infty}{\sim} \sin(kr - \tfrac{1}{2}\ell\pi) \tag{1.10}$$

and

$$c_\ell(kr) = -kr n_\ell(kr) = (-1)^\ell \left(\frac{\pi kr}{2}\right)^{\frac{1}{2}} J_{-\ell-\frac{1}{2}}(kr) \underset{r\to\infty}{\sim} \cos(kr - \tfrac{1}{2}\ell\pi)\,. \tag{1.11}$$

The remaining quantity in (1.9) is the partial wave phase shift $\delta_\ell(k)$ which is a real function of the wave number k when the reduced potential $U(r)$, energy E and angular momentum ℓ are real.

It is also convenient to introduce the S-matrix, whose matrix elements are defined in terms of the phase shifts. We first note that (1.8) satisfied by $u_\ell(r)$ is homogeneous so that $u_\ell(r)$ is only defined up to an arbitrary multiplicative complex normalization factor N. Hence it follows from (1.9) that

$$u_\ell^N(r) \underset{r\to\infty}{\sim} N[s_\ell(kr) + c_\ell(kr)\tan\delta_\ell(k)] \tag{1.12}$$

is also a solution of (1.8) for arbitrary N. If we choose $N = -2\mathrm{i}\cos\delta_\ell \exp(\mathrm{i}\delta_\ell)$ then we can rewrite (1.12) as

$$u_\ell(r) \underset{r\to\infty}{\sim} \exp(-\mathrm{i}\theta_\ell) - \exp(\mathrm{i}\theta_\ell)S_\ell(k)\,, \tag{1.13}$$

where $\theta_\ell = kr - \frac{1}{2}\ell\pi$. The quantity $S_\ell(k)$ in (1.13) is then a diagonal element of the S-matrix defined by

$$S_\ell(k) = \exp[2\mathrm{i}\delta_\ell(k)] = \frac{1 + \mathrm{i}K_\ell(k)}{1 - \mathrm{i}K_\ell(k)}\,, \tag{1.14}$$

where we have also introduced the K-matrix, whose diagonal elements are defined by

$$K_\ell(k) = \tan\delta_\ell(k)\,. \tag{1.15}$$

We see from (1.9) that the phase shift, and hence the K-matrix, is a measure of the departure of the radial wave function from the form it has when the potential $U(r)$ is zero.

We can obtain useful integral expressions for the K-matrix and the phase shift. We consider the solution $v_\ell(r)$ of the radial Schrödinger equation, obtained from (1.8) by setting the potential $U(r) = 0$. Hence $v_\ell(r)$ satisfies the equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) v_\ell(r) = 0\,. \tag{1.16}$$

We choose $v_\ell(r)$ to be the regular solution of this equation, given by

$$v_\ell(r) = s_\ell(r)\,, \tag{1.17}$$

where $s_\ell(r)$ is defined by (1.10). We then premultiply (1.8) by $v_\ell(r)$, premultiply (1.16) by $u_\ell(r)$ and then integrate the difference of these two equations from $r = 0$ to ∞. We obtain

$$\int_0^\infty \left(v_\ell(r) \frac{\mathrm{d}^2 u_\ell}{\mathrm{d}r^2} - u_\ell(r) \frac{\mathrm{d}^2 v_\ell}{\mathrm{d}r^2} \right) \mathrm{d}r = \int_0^\infty v_\ell(r) U(r) u_\ell(r) \mathrm{d}r \,. \tag{1.18}$$

The left-hand side of this equation can be evaluated using Green's formula and the boundary conditions satisfied by $u_\ell(r)$ and $v_\ell(r)$, given by (1.9) and (1.10), yielding the result $-k \tan \delta_\ell(k)$. We then substitute for $v_\ell(r)$ in terms of $j_\ell(kr)$ on the right-hand side of (1.18) using (1.10) and (1.17). Combining these results we find that (1.18) reduces to

$$K_\ell(k) = \tan \delta_\ell(k) = -\int_0^\infty j_\ell(kr) U(r) u_\ell(r) r \mathrm{d}r \,, \tag{1.19}$$

which is an exact integral expression for the K-matrix element and the phase shift. If the potential $U(r)$ is weak or the scattered particle is moving fast, the distortion of $u_\ell(r)$ in (1.19) will be small. In this case $u_\ell(r)$ can be replaced by $v_\ell(r)$ and, after using (1.10) and (1.17), we find that (1.19) reduces to

$$K_\ell^B(k) = \tan \delta_\ell^B(k) = -k \int_0^\infty U(r) j_\ell^2(kr) r^2 \mathrm{d}r \,. \tag{1.20}$$

This is the first Born approximation for the K-matrix element and the phase shift which we will use when we discuss effective range theory for long-range potentials, in Sect. 1.4.2.

We will also need to consider solutions of (1.8) satisfying the following orthonormality relation

$$\int_0^\infty \left[u_\ell^N(k, r) \right]^* u_\ell^N(k', r) \mathrm{d}r = \delta(E - E') \,, \tag{1.21}$$

where we have displayed explicitly the dependence of the solution $u_\ell^N(r)$ on the wave number k and where $[u_\ell^N(k, r)]^*$ is the complex conjugate of $u_\ell^N(k, r)$. Also in (1.21) we have introduced the Dirac δ-function [263], which can be defined by the relations

$$\delta(x) = 0 \text{ for } x \neq 0 \,, \quad \int_{-\infty}^\infty \delta(x) \mathrm{d}x = 1 \,. \tag{1.22}$$

Of particular importance in applications are the following three solutions satisfying (1.21), corresponding to different choices of the normalization factor N in (1.12). Using (C.53) and (C.54) we define the real solution

$$u_\ell(k, r) \underset{r \to \infty}{\sim} \left(\frac{2}{\pi k} \right)^{\frac{1}{2}} [\sin \theta_\ell + \cos \theta_\ell K_\ell(k)] \left[1 + K_\ell^2(k) \right]^{-\frac{1}{2}} \,, \tag{1.23}$$

the outgoing wave solution

$$u_\ell^+(k, r) \underset{r \to \infty}{\sim} \left(\frac{2}{\pi k} \right)^{\frac{1}{2}} \left[\sin \theta_\ell + (2\mathrm{i})^{-1} \exp(\mathrm{i}\theta_\ell) T_\ell(k) \right] \tag{1.24}$$

and the ingoing wave solution

$$u_\ell^-(k,r) \underset{r\to\infty}{\sim} \left(\frac{2}{\pi k}\right)^{\frac{1}{2}} \left[\sin\theta_\ell - (2\mathrm{i})^{-1}\exp(-\mathrm{i}\theta_\ell)T_\ell^*(k)\right], \tag{1.25}$$

where in (1.24) and (1.25) we have introduced the T-matrix element $T_\ell(k)$ which is related to the K-matrix and the S-matrix elements by

$$T_\ell(k) = \frac{2\mathrm{i}K_\ell(k)}{1-\mathrm{i}K_\ell(k)} = S_\ell(k) - 1\,. \tag{1.26}$$

It is clear that if the reduced potential $U(r)$ is zero so that there is no scattering, then the phase shift $\delta_\ell(k) = 0$ and hence $S_\ell(k) = 1$ and $T_\ell(k) = 0$.

We are now in a position to determine an expression for the scattering amplitude in terms of the phase shifts. To achieve this we expand the plane wave term in (1.2) in partial waves and equate it with the asymptotic form of (1.7). The required expansion of the plane wave term in terms of Legendre polynomials, discussed in Appendix B.1, is

$$\mathrm{e}^{\mathrm{i}kz} = \sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^\ell j_\ell(kr)P_\ell(\cos\theta)\,. \tag{1.27}$$

Since the second term in (1.2) contributes only to the outgoing spherical wave in (1.7), we can determine the coefficients $B_\ell(k)$ by equating the coefficients of the ingoing wave $\mathrm{e}^{-\mathrm{i}kr}$ in (1.7) and (1.27). Using (1.9), (1.10), and (1.11) we find that

$$B_\ell(k) = k^{-1}(2\ell+1)\mathrm{i}^\ell\cos\delta_\ell(k)\exp[\mathrm{i}\delta_\ell(k)]\,. \tag{1.28}$$

Substituting this result into (1.7) and comparing with (1.2), then gives the following expression for the scattering amplitude:

$$f(\theta,\phi) = \frac{1}{2\mathrm{i}k}\sum_{\ell=0}^{\infty}(2\ell+1)\{\exp[2\mathrm{i}\delta_\ell(k)]-1\}P_\ell(\cos\theta)\,. \tag{1.29}$$

We notice that the scattering amplitude does not depend on the azimuthal angle ϕ since we have restricted our consideration to an incident beam in the z-direction scattering from a spherically symmetric potential. Also, for short-range potentials considered in this section, $\delta_\ell(k)$ tends rapidly to zero as ℓ tends to ∞ and hence the summation in (1.29) gives accurate results at low energies when only a few terms are retained.

An expression for the total cross section is obtained by substituting (1.29) into (1.5). We obtain

$$\sigma_{\mathrm{tot}} = \sum_{\ell=0}^{\infty}\sigma_\ell = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell(k)\,, \tag{1.30}$$

where σ_ℓ is called the partial wave cross section. Also substituting (1.29) into (1.6) yields the following expression for the momentum transfer cross section:

$$\sigma_M = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(\ell+1)\sin^2[\delta_{\ell+1}(k)-\delta_\ell(k)]\,. \tag{1.31}$$

Finally, we observe that the imaginary part of the scattering amplitude in the forward direction can be related to the total cross section. Since $P_\ell(1) = 1$ we obtain from (1.29)

$$\mathrm{Im}\, f(\theta=0,\phi) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell(k)\,. \tag{1.32}$$

Comparing this result with (1.30) gives immediately

$$\sigma_{\mathrm{tot}} = \frac{4\pi}{k}\mathrm{Im}\, f(\theta=0,\phi)\,, \tag{1.33}$$

which is known as the optical theorem [316]. This result, which can be generalized to multichannel collisions, can be shown to be a direct consequence of conservation of probability.

We conclude our discussion of scattering by a short-range potential by observing that the procedure of adopting a partial wave analysis of the wave function and the scattering amplitude is appropriate at low and intermediate energies when only a relatively small number of partial wave phase shifts are significantly different from zero. This situation is relevant to our discussion of R-matrix theory of atomic collisions in Part II of this monograph. On the other hand, at high energies this procedure breaks down because of the large number of partial waves which are required to determine the cross section accurately. It is then necessary to obtain a solution of the Schrödinger equation (1.1) which directly takes account of the boundary condition of the problem. This is the basis of the procedure introduced by Lippmann and Schwinger [600]. In this procedure the Schrödinger equation (1.1) is written in the form

$$(E-H_0)\psi(\mathbf{r}) = V(\mathbf{r})\psi(\mathbf{r})\,. \tag{1.34}$$

We can then solve this equation to yield a solution with the required asymptotic form by introducing the Green's function for the operator on the left-hand side. We obtain the formal solution

$$\psi^{\pm} = \phi + \frac{1}{E-H_0\pm \mathrm{i}\epsilon}V\psi^{\pm}\,, \tag{1.35}$$

where the term $\pm\mathrm{i}\epsilon$ in the denominator defines the contour of integration past the singularity $E = H_0$ and ϕ is the solution of the free-particle wave equation

$$(E-H_0)\phi = 0\,. \tag{1.36}$$

The Lippmann–Schwinger equation (1.35) is the basic integral equation of time-independent scattering theory and an iterative solution of this equation yields the Born series expansion. The solution of this equation is discussed in detail in the monographs by Burke [158] and Burke and Joachain [171].

1.2 Scattering by a Coulomb Potential

The discussion in the previous section must be modified when a long-range Coulomb potential is present in addition to the short-range potential $V(\mathbf{r})$.

We consider first scattering by a pure Coulomb potential acting between a particle of unit mass and charge number Z_1 and a particle of infinite mass and charge number Z_2. The time-independent Schrödinger equation is then

$$\left(-\frac{1}{2}\nabla^2 + V_c(\mathbf{r})\right)\psi_c(\mathbf{r}) = E\psi_c(\mathbf{r})\,, \tag{1.37}$$

where the Coulomb potential

$$V_c(\mathbf{r}) = \frac{Z_1 Z_2}{r}\,, \tag{1.38}$$

in atomic units. The solution of (1.37) was obtained by Gordon [403] and Temple [913] by introducing parabolic coordinates

$$\zeta = r - z, \quad \xi = r + z, \quad \phi = \tan^{-1}\frac{y}{x}\,. \tag{1.39}$$

In these coordinates the Laplacian becomes

$$\nabla^2 = \frac{4}{\zeta+\xi}\left[\frac{\partial}{\partial\zeta}\left(\zeta\frac{\partial}{\partial\zeta}\right) + \frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right)\right] + \frac{1}{\zeta\xi}\frac{\partial^2}{\partial\phi^2}\,. \tag{1.40}$$

The solution of (1.37), corresponding to an incident wave in the z-direction and an outgoing scattered wave, can then be written as

$$\psi_c(\mathbf{r}) = \exp(-\tfrac{1}{2}\pi\eta)\Gamma(1+\mathrm{i}\eta)\mathrm{e}^{\mathrm{i}kz}\,{}_1F_1(-\mathrm{i}\eta;\,1;\,\mathrm{i}k\zeta)\,, \tag{1.41}$$

where

$$\eta = \frac{\beta}{2k} = \frac{Z_1 Z_2}{k}\,, \tag{1.42}$$

and $\Gamma(z)$ is the gamma function. Also the function ${}_1F_1$ is defined by

$$\begin{aligned} {}_1F_1(a;b;z) &= 1 + \frac{a}{b}z + \frac{a(a+1)}{b(b+1)}\frac{z^2}{2!} + \cdots \\ &= \sum_{n=0}^{\infty}\frac{\Gamma(a+n)\Gamma(b)}{\Gamma(a)\Gamma(b+n)}\frac{z^n}{n!} \end{aligned} \tag{1.43}$$

and is related to the confluent hypergeometric function $M_{k,m}(z)$, defined by Whittaker and Watson [964], by

$$M_{k,m}(z) = z^{m+1/2} \exp(-\tfrac{1}{2}z)\ {}_1F_1(\tfrac{1}{2} + m - k; 2m + 1; z)\,. \tag{1.44}$$

The asymptotic form of ${}_1F_1$ can be obtained by writing

$${}_1F_1(a; b; z) = W_1(a; b; z) + W_2(a; b; z)\,, \tag{1.45}$$

where

$$W_1(a; b; z) \underset{|z|\to\infty}{\sim} \frac{\Gamma(b)}{\Gamma(b-a)}(-z)^{-a} v(a; a - b + 1; -z), \quad -\pi < \arg(-z) < \pi \tag{1.46}$$

and

$$W_2(a; b; z) \underset{|z|\to\infty}{\sim} \frac{\Gamma(b)}{\Gamma(a)} \mathrm{e}^z z^{a-b} v(1 - a; b - a; z), \quad -\pi < \arg(z) < \pi\,, \tag{1.47}$$

where v has the asymptotic expansion

$$\begin{aligned} v(\alpha; \beta; z) &= 1 + \frac{\alpha\beta}{z} + \frac{\alpha(\alpha+1)\beta(\beta+1)}{2!z^2} + \cdots \\ &= \sum_{n=0}^{\infty} \frac{\Gamma(n+\alpha)\Gamma(n+\beta)}{\Gamma(\alpha)\Gamma(\beta)} \frac{(z)^{-n}}{n!}\,. \end{aligned} \tag{1.48}$$

The W_1 term corresponds to the Coulomb-modified incident wave and the W_2 term to the outgoing scattered wave in $\psi_c(\mathbf{r})$. Thus we can write

$$\psi_c(\mathbf{r}) \underset{|r-z|\to\infty}{\sim} I + f_c(\theta) J\,, \tag{1.49}$$

where

$$I = \exp[\mathrm{i}kz + \mathrm{i}\eta \ln(k\zeta)] \left(1 + \frac{\eta^2}{\mathrm{i}k\zeta} + \cdots\right) \tag{1.50}$$

and

$$J = r^{-1} \exp[\mathrm{i}kr - \mathrm{i}\eta \ln(2kr)] \left(1 + \frac{(1+\mathrm{i}\eta)^2}{\mathrm{i}k\zeta} + \cdots\right). \tag{1.51}$$

The Coulomb scattering amplitude is then given by

$$f_c(\theta) = -\frac{\eta}{2k \sin^2(\theta/2)} \exp[-\mathrm{i}\eta \ln \sin^2(\theta/2) + 2\mathrm{i}\sigma_0]\,, \tag{1.52}$$

where

$$\sigma_0 = \arg \Gamma(1 + \mathrm{i}\eta)\,, \tag{1.53}$$

and the differential cross section is given by

$$\frac{\mathrm{d}\sigma_c}{\mathrm{d}\Omega} = |f_c(\theta)|^2 = \frac{\eta^2}{4k^2 \sin^4(\theta/2)} = \frac{(Z_1 Z_2)^2}{16E^2 \sin^4(\theta/2)}\,. \tag{1.54}$$

This result was first obtained by Rutherford [802] using classical mechanics to describe the scattering of α-particles by nuclei. Since the differential cross section diverges like θ^{-4} at small θ, the total Coulomb cross section obtained by integrating over all scattering angles is infinite. A further difference from the result obtained in Sect. 1.1 for scattering by short-range potentials is the distortion of both the incident and scattered waves, defined by (1.50) and (1.51), by logarithmic phase factors. These phase factors are a direct consequence of the long-range nature of the Coulomb potential. However, we see that they do not affect the form of the differential cross section for scattering by a pure Coulomb potential given by (1.54).

For electron–ion scattering problems of practical interest, the interaction potential experienced by the scattered electron is not pure Coulombic but is modified at short distances by the interaction of the scattered electron with the target electrons. In this case it is appropriate at low scattering energies to make a partial wave analysis of the scattering wave function in spherical polar coordinates, as in Sect. 1.1 where we considered short-range potentials.

We commence our discussion by making a partial wave analysis of the pure Coulomb scattering problem. Following (1.7) we expand the wave function in (1.37) in partial waves as

$$\psi_c(\mathbf{r}) = \sum_{\ell=0}^{\infty} B_\ell^c(k) r^{-1} u_\ell^c(r) P_\ell(\cos\theta)\,, \tag{1.55}$$

where $u_\ell^c(r)$ satisfies the radial Schrödinger equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U_c(r) + k^2\right) u_\ell^c(r) = 0\,, \tag{1.56}$$

and where

$$U_c(r) = 2V_c(r) = \frac{2Z_1 Z_2}{r} \tag{1.57}$$

is the reduced Coulomb potential. Equation (1.56) is the Coulomb wave equation that has been discussed extensively in the literature (e.g. by Yost et al. [984], Hull and Breit [479], Fröberg [343] and Chap. 14 of Abramowitz and Stegun [1]). The

solutions of this equation, which are regular and irregular at the origin, known as Coulomb wave functions, are defined, respectively, by

$$\begin{aligned} F_\ell(\eta, kr) &= C_\ell(\eta)\mathrm{e}^{\mathrm{i}kr}(kr)^{\ell+1}\ {}_1F_1(\ell+1+\mathrm{i}\eta; 2\ell+2; -2\mathrm{i}kr) \\ &\underset{r\to\infty}{\sim} \sin(kr - \tfrac{1}{2}\ell\pi - \eta\ln 2kr + \sigma_\ell) \end{aligned} \tag{1.58}$$

and

$$\begin{aligned} G_\ell(\eta, kr) &= \mathrm{i}C_\ell(\eta)\mathrm{e}^{\mathrm{i}kr}(kr)^{\ell+1}\,[W_1(\ell+1+\mathrm{i}\eta; 2\ell+2; -2\mathrm{i}kr) \\ &\quad - W_2(\ell+1+\mathrm{i}\eta; 2\ell+2; -2\mathrm{i}kr)] \\ &\underset{r\to\infty}{\sim} \cos(kr - \tfrac{1}{2}\ell\pi - \eta\ln 2kr + \sigma_\ell)\,, \end{aligned} \tag{1.59}$$

where η is defined by (1.42). Also in (1.58) and (1.59)

$$\begin{aligned} C_\ell(\eta) &= \frac{2^\ell \exp(-\frac{1}{2}\pi\eta)|\Gamma(\ell+1+\mathrm{i}\eta)|}{\Gamma(2\ell+2)} \\ &= C_0(\eta)\frac{2^\ell}{\Gamma(2\ell+2)}\prod_{s=1}^{\ell}(s^2+\eta^2)^{1/2}\,, \end{aligned} \tag{1.60}$$

with

$$C_0(\eta) = \left(\frac{2\pi\eta}{\mathrm{e}^{2\pi\eta}-1}\right)^{1/2}, \tag{1.61}$$

and σ_ℓ is the Coulomb phase shift

$$\sigma_\ell = \arg\Gamma(\ell+1+\mathrm{i}\eta)\,. \tag{1.62}$$

In order to determine the coefficients $B_\ell^c(k)$ in (1.55), we choose $u_\ell^c(r)$ to be the regular Coulomb wave function $F_\ell(\eta, kr)$ and require that $\psi_c(\mathbf{r})$ has the normalization defined by (1.41). Using the orthogonality properties of the Legendre polynomials and matching $\psi_c(\mathbf{r})$, given by (1.41) and (1.55), in the neighbourhood of $r = 0$ gives

$$B_\ell^c(k) = k^{-1}(2\ell+1)\mathrm{i}^\ell\exp(\mathrm{i}\sigma_\ell)\,, \tag{1.63}$$

so that

$$\psi_c(\mathbf{r}) = \sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^\ell\exp(\mathrm{i}\sigma_\ell)(kr)^{-1}F_\ell(\eta, kr)P_\ell(\cos\theta)\,. \tag{1.64}$$

This equation reduces to the expansion of the plane wave given by (1.27) when $\eta = 0$.

We now define the Coulomb S-matrix, in analogy with our discussion of scattering by a short-range potential, by considering the asymptotic form of the ℓth partial wave component of $\psi_c(\mathbf{r})$. From (1.58) and (1.64) this component has the asymptotic form

$$F_\ell(\eta, kr) \underset{r\to\infty}{\sim} N\left[\exp(-\mathrm{i}\theta_\ell^c) - \exp(\mathrm{i}\theta_\ell^c) S_\ell^c(k)\right], \tag{1.65}$$

where the normalization factor $N = -\exp(-\mathrm{i}\sigma_\ell)/2\mathrm{i}$, the phase factor $\theta_\ell^c = kr - \frac{1}{2}\ell\pi - \eta \ln 2kr$ and the Coulomb S-matrix $S_\ell^c(k)$ is given by

$$S_\ell^c(k) = \exp(2\mathrm{i}\sigma_\ell) = \frac{\Gamma(\ell + 1 + \mathrm{i}\eta)}{\Gamma(\ell + 1 - \mathrm{i}\eta)}. \tag{1.66}$$

It follows from the asymptotic properties of the Gamma function that the Coulomb S-matrix is analytic in the entire complex k-plane except for poles where $\ell+1+\mathrm{i}\eta = -\bar{n}$ with $\bar{n} = 0, 1, 2, \ldots$. Using (1.42) we see that the corresponding values of k are given by

$$k_{\bar{n}} = -\mathrm{i}\frac{Z_1 Z_2}{\bar{n} + \ell + 1}, \quad \bar{n} = 0, 1, 2, \ldots. \tag{1.67}$$

Thus for an attractive Coulomb potential ($Z_1 Z_2 < 0$) the poles of $S_\ell^c(k)$ lie on the positive imaginary axis of the complex k-plane. At these poles it follows from (1.65) that the wave function decays exponentially asymptotically and hence these poles correspond to the familiar bound states with energies

$$E_n = -\frac{1}{2}\frac{Z_1^2 Z_2^2}{n^2}, \quad n = \ell + 1,\ \ell + 2, \ldots, \tag{1.68}$$

where we have introduced the principal quantum number $n = \bar{n} + \ell + 1$. The location of poles in the S-matrix in the complex k-plane, corresponding to bound states and resonances, is discussed further in Sect. 1.3.

We now consider the situation where an additional short-range potential $V(r)$, which vanishes asymptotically faster than r^{-1}, is added to the Coulomb potential. Again, carrying out a partial wave analysis as in (1.7), we expand the total wave function as follows:

$$\psi(\mathbf{r}) = \sum_{\ell=0}^{\infty} B_\ell^s(k) r^{-1} u_\ell^s(r) P_\ell(\cos\theta), \tag{1.69}$$

where $u_\ell^s(r)$ satisfies the radial Schrödinger equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) - U_c(r) + k^2\right) u_\ell^s(r) = 0, \tag{1.70}$$

where $U(r) = 2V(r)$ and, following (1.57), the reduced Coulomb potential $U_c(r) = 2V_c(r) = 2Z_1Z_2/r$. For large r, the potential $U(r)$ can be neglected compared with $U_c(r)$ and (1.70) then reduces to the Coulomb equation (1.56). The solution of (1.70) that is regular at the origin can thus be written asymptotically as a linear combination of the regular and irregular Coulomb wave functions $F_\ell(\eta, kr)$ and $G_\ell(\eta, kr)$. Hence, in analogy with (1.9), we look for a solution satisfying the boundary conditions

$$\begin{aligned} u_\ell^s(0) &\underset{r\to 0}{\sim} nr^{\ell+1}\,, \\ u_\ell^s(r) &\underset{r\to\infty}{\sim} F_\ell(\eta, kr) + G_\ell(\eta, kr)\tan\delta_\ell(k)\,. \end{aligned} \tag{1.71}$$

The quantity $\delta_\ell(k)$ defined by these equations is the phase shift due to the short-range potential $V(r)$ in the presence of the Coulomb potential $V_c(r)$. We note that $\delta_\ell(k)$ vanishes when the short-range potential is not present and contains all the information necessary to describe the non-Coulombic part of the scattering.

The coefficients $B_\ell^s(k)$ in (1.69) are determined by equating the coefficients of the ingoing wave in (1.49) and (1.69). This gives

$$B_\ell^s(k) = k^{-1}(2\ell+1)\mathrm{i}^\ell \cos\delta_\ell(k)\exp\{\mathrm{i}[\sigma_\ell + \delta_\ell(k)]\}\,. \tag{1.72}$$

Substituting this result into (1.69) then gives

$$\begin{aligned} \psi(\mathbf{r}) \underset{r\to\infty}{\sim} \psi_c(\mathbf{r}) + (2kr)^{-1}\sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^\ell \exp(2\mathrm{i}\sigma_\ell)\{\exp[2\mathrm{i}\delta_\ell(k)] - 1\}H_\ell^+(\eta, kr) \\ \times\, P_\ell(\cos\theta)\,, \end{aligned} \tag{1.73}$$

where we have defined the function

$$H_\ell^+(\eta, \rho) = \exp(\mathrm{i}\sigma_\ell)\,[F_\ell(\eta, \rho) + \mathrm{i}G_\ell(\eta, \rho)]\,. \tag{1.74}$$

We then find that

$$\psi(\mathbf{r}) \underset{r\to\infty}{\sim} \exp[\mathrm{i}(kz + \eta\ln k\zeta)] + \big[f_c(\theta) + f_s(\theta)\big]\frac{\exp[\mathrm{i}(kr - \eta\ln 2kr)]}{r}\,, \tag{1.75}$$

where $f_c(\theta)$ is the Coulomb scattering amplitude given by (1.52) and $f_s(\theta)$ is the scattering amplitude arising from the additional short-range potential $V(r)$. We find that

$$f_s(\theta) = \frac{1}{2\mathrm{i}k}\sum_{\ell=0}^{\infty}(2\ell+1)\exp(2\mathrm{i}\sigma_\ell)\{\exp[2\mathrm{i}\delta_\ell(k)] - 1\}P_\ell(\cos\theta)\,, \tag{1.76}$$

which is analogous to the result given by (1.29) when there is only a short-range potential.

The differential cross section can be obtained in the usual way from (1.75) by calculating the outward flux of particles scattered through a spherical surface $r^2 \mathrm{d}\Omega$ for large r per unit solid angle divided by the incident flux. This gives

$$\begin{aligned} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= |f_c(\theta) + f_s(\theta)|^2 \\ &= |f_c(\theta)|^2 + |f_s(\theta)|^2 + 2\mathrm{Re}\left[f_c^*(\theta) f_s(\theta)\right] . \end{aligned} \tag{1.77}$$

At small scattering angles the Coulomb scattering amplitude will dominate the differential cross section giving a θ^{-4} singularity in the forward direction. However, at larger scattering angles $f_s(\theta)$ becomes relatively more important and information on the phase of $f_s(\theta)$ can be obtained from intermediate angles when the interference term in (1.77) involving both $f_c(\theta)$ and $f_s(\theta)$ is important.

Finally we remark that, as is the case for pure Coulomb scattering, because of the divergence in the forward direction the total cross section obtained by integrating (1.77) over all scattering angles is infinite.

1.3 Analytic Properties of the *S*-Matrix

In this section we consider the analytic properties of the partial wave S-matrix, defined by (1.14), in the complex momentum plane. We show that the poles in the S-matrix lying on the positive imaginary k-axis correspond to bound states while poles lying in the lower half k-plane close to the positive real k-axis correspond to resonances. We also derive an expression for the behaviour of the phase shift and the cross section when the energy of the scattered particle is in the neighbourhood of these poles.

We consider the solution $u_\ell(r)$ of the radial Schrödinger equation (1.8) describing the scattering of a particle by a spherically symmetric reduced potential $U(r)$ which we assume is less singular than r^{-2} at the origin and vanishes faster than r^{-3} at infinity. Hence we assume

$$\int_0^\infty r|U(r)|\mathrm{d}r < \infty \tag{1.78}$$

and

$$\int_0^\infty r^2|U(r)|\mathrm{d}r < \infty , \tag{1.79}$$

so that the solution $u_\ell(r)$ satisfies the boundary conditions (1.9).

Following Jost [515], we introduce two solutions $f_\ell(\pm k, r)$ of (1.8) defined by the relations

$$\lim_{r\to\infty} \mathrm{e}^{\pm \mathrm{i}kr} f_\ell(\pm k, r) = 1 . \tag{1.80}$$

These boundary conditions define $f_\ell(k,r)$ uniquely only in the lower half k-plane and $f_\ell(-k,r)$ uniquely only in the upper half k-plane. If the potential satisfies inequalities (1.78) and (1.79) then $f_\ell(k,r)$ is an analytic function of k when $\mathrm{Im}\ k < 0$ for all r, while $f_\ell(-k,r)$ is correspondingly an analytic function of k when $\mathrm{Im}\ k > 0$ [52]. These regions of analyticity can be extended if we impose stronger conditions on the potential. Thus if

$$I(\mu) = \int_0^\infty \mathrm{e}^{\mu r}|U(r)|\mathrm{d}r < \infty, \quad \mu \text{ real} > 0\,, \tag{1.81}$$

then $f_\ell(k,r)$ is analytic for $\mathrm{Im}\, k < \mu/2$ while $f_\ell(-k,r)$ is analytic for $\mathrm{Im}\, k > -\mu/2$. Further, if the potential can be written as a superposition of Yukawa potentials

$$U(r) = \int_{\mu_0}^\infty \rho(\mu)\frac{\mathrm{e}^{-\mu r}}{r}\mathrm{d}\mu\,, \tag{1.82}$$

where $\rho(\mu)$ is a weight function and $\mu_0 > 0$, then $f_\ell(k,r)$ will be analytic in the complex k-plane apart from a branch cut on the positive imaginary k-axis from $k = \mathrm{i}\mu_0/2$ to $\mathrm{i}\infty$ while $f_\ell(-k,r)$ will be analytic in the complex k-plane apart from a branch cut from $k = -\mathrm{i}\mu_0/2$ to $-\mathrm{i}\infty$. These branch cuts are called Yukawa cuts. Finally, if the potential vanishes identically beyond a certain distance a_0 then $I(\mu)$ defined by (1.81) is finite for all μ so that $f_\ell(\pm k,r)$ are analytic functions of k in the open k-plane for all fixed values of r, that is, they are entire functions of k.

We can express the physical solution of (1.8), defined by the boundary conditions (1.9), as a linear combination of $f_\ell(\pm k,r)$. Let us normalize this solution so that it satisfies

$$\lim_{r\to 0} r^{-l-1}u_\ell(r) = 1\,. \tag{1.83}$$

From a theorem proved by Poincaré [749], the absence of a k-dependence in this boundary condition implies that this solution is an entire function of k. The Jost functions [515] are then defined by

$$\tilde{f}_\ell(\pm k) = W[f_\ell(\pm k,r), u_\ell(r)]\,, \tag{1.84}$$

where the Wronskian $W[f,g] = fg' - f'g$ and where the primes denote the derivatives with respect to r. It is straightforward to show from the differential equation (1.8) satisfied by $f_\ell(\pm k,r)$ and $u_\ell(r)$ that the Wronskian is independent of r. It is also convenient to introduce other Jost functions by the equation

$$f_\ell(\pm k) = \frac{k^\ell \exp(\pm\frac{1}{2}\mathrm{i}\ell\pi)}{(2\ell+1)!!}\tilde{f}_\ell(\pm k)\,. \tag{1.85}$$

The functions $f_\ell(+k)$ and $f_\ell(-k)$ are continuous at $k = 0$ and approach unity at large $|k|$ for $\mathrm{Im}\, k \le 0$ and ≥ 0, respectively.

We now use the relations

$$W[f_\ell(\pm k, r),\, f_\ell(\mp k, r)] = \pm 2\mathrm{i}k\,,$$
$$W[f_\ell(\pm k, r),\, f_\ell(\pm k, r)] = 0\,, \tag{1.86}$$

which follow from (1.80) and the definition of the Wronskian, to write $u_\ell(r)$ in the form

$$u_\ell(r) = \frac{1}{2\mathrm{i}k}[\tilde{f}_\ell(k) f_\ell(-k, r) - \tilde{f}_\ell(-k) f_\ell(k, r)]\,. \tag{1.87}$$

Comparing this equation with the asymptotic form (1.13) and using (1.80) then yields the following expression for the S-matrix elements:

$$S_\ell(k) = \mathrm{e}^{\mathrm{i}\pi\ell}\,\frac{\tilde{f}_\ell(k)}{\tilde{f}_\ell(-k)} = \frac{f_\ell(k)}{f_\ell(-k)}\,. \tag{1.88}$$

This equation relates the analytic properties of the S-matrix with the simpler analytic properties of the Jost functions.

In order to study the analytic properties of the Jost functions further we return to (1.8) satisfied by the functions $f_\ell(\pm k, r)$. In particular we consider

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2\right) f_\ell(-k, r) = 0\,. \tag{1.89}$$

We now take the complex conjugate of this equation, which gives

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^{*2}\right) f_\ell^*(-k, r) = 0\,, \tag{1.90}$$

where we have assumed that r, ℓ and $U(r)$ are real but k can take complex values. In addition, it follows from (1.89) that $f_\ell(k^*, r)$ is a solution of

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^{*2}\right) f_\ell(k^*, r) = 0\,. \tag{1.91}$$

Now from (1.80)

$$f_\ell^*(-k, r) \underset{r\to\infty}{\sim} \exp(-\mathrm{i}k^* r) \tag{1.92}$$

and

$$f_\ell(k^*, r) \underset{r\to\infty}{\sim} \exp(-\mathrm{i}k^* r)\,, \tag{1.93}$$

so that $f_\ell^*(-k,r)$ and $f_\ell(k^*,r)$ satisfy the same boundary conditions. Since these functions also satisfy the same differential equation, namely (1.90) and (1.91), respectively, they are equal for all r, for all points in the upper half k-plane and for all other points which admit an analytic continuation from the upper half k-plane. Hence in this region

$$f_\ell^*(-k,r) = f_\ell(k^*,r) \tag{1.94}$$

and thus from (1.84) the Jost functions satisfy

$$\tilde{f}_\ell^*(-k) = \tilde{f}_\ell(k^*)\,. \tag{1.95}$$

Combining this result with (1.88) we find that the S-matrix satisfies the following symmetry relation

$$S_\ell(k)S_\ell(-k) = \mathrm{e}^{2\mathrm{i}\pi\ell}\,\frac{\tilde{f}_\ell(k)}{\tilde{f}_\ell(-k)}\,\frac{\tilde{f}_\ell(-k)}{\tilde{f}_\ell(k)} = \mathrm{e}^{2\mathrm{i}\pi\ell} \tag{1.96}$$

and the unitarity relation

$$S_\ell(k)S_\ell^*(k^*) = \frac{\tilde{f}_\ell(k)}{\tilde{f}_\ell(-k)}\,\frac{\tilde{f}_\ell^*(k^*)}{\tilde{f}_\ell^*(-k^*)} = 1\,. \tag{1.97}$$

Also, from (1.96) and (1.97) we obtain the reflection relation

$$S_\ell(k) = \mathrm{e}^{2\mathrm{i}\pi\ell}\,S_\ell^*(-k^*)\,. \tag{1.98}$$

From (1.97), it follows that if k is real then the S-matrix has unit modulus and can thus be expressed in terms of a real phase shift $\delta_\ell(k)$ as

$$S_\ell(k) = \exp[2\mathrm{i}\delta_\ell(k)]\,, \tag{1.99}$$

in agreement with (1.14). In addition it follows from (1.98) that if the S-matrix has a pole at the point k, then it also has a pole at the point $-k^*$ and from (1.96) and (1.97) it has zeros at the points $-k$ and k^*. Thus the poles and zeros of the S-matrix are symmetrically situated with respect to the imaginary k-axis.

In order to determine the physical significance of poles in the S-matrix we note from (1.84) that the Jost functions $\tilde{f}_\ell(\pm k)$ are finite for all finite k. Hence it follows from (1.88) that a pole in the S-matrix must correspond to a zero in $\tilde{f}_\ell(-k)$ rather than a pole in $\tilde{f}_\ell(k)$. Substituting this result into (1.87) and using (1.80) shows that the physical solution of (1.8) corresponding to a pole in the S-matrix has the following asymptotic form:

$$u_\ell(r) \underset{r\to\infty}{\sim} N\mathrm{e}^{\mathrm{i}kr}\,, \tag{1.100}$$

where N is a normalization factor. When k is in the upper half k-plane, it follows from (1.100) that the corresponding wave function vanishes exponentially and hence is normalizable. Since the Hamiltonian is hermitian, all normalizable wave functions must correspond to real energy eigenvalues and hence the corresponding value of k^2 must be real. This shows that if a pole in the S-matrix occurs in the upper half k-plane in the region of analyticity connected to the physical real k-axis it must lie on the positive imaginary axis. If we write $k = \mathrm{i}\kappa$, where κ is real and positive, then (1.100) becomes

$$u_\ell(r) \underset{r\to\infty}{\sim} N\mathrm{e}^{-\kappa r}\,, \tag{1.101}$$

which clearly corresponds to a bound state with binding energy $-\kappa^2/2$. In the lower half k-plane the wave function defined by (1.100) diverges exponentially and thus cannot be normalized. The above arguments based on the hermiticity of the Hamiltonian then break down and the corresponding poles are then no longer confined to the imaginary k-axis.

We present in Fig. 1.1 a possible distribution of S-matrix poles in the complex k-plane. For potentials satisfying (1.78) and (1.79), only a finite number of bound states can be supported and these give rise to the poles lying on the positive imaginary axis in this figure. However, an infinite number of poles can occur in the lower half k-plane. If they do not lie on the negative imaginary k-axis, they occur in pairs symmetric with respect to this axis, as discussed above. If they lie on the negative imaginary k-axis, they are often referred to as virtual state poles. Poles lying in the lower half k-plane and close to the real positive k-axis give rise to resonance effects in the cross section which will be discussed below. The corresponding resonance states, defined by the outgoing wave boundary condition (1.100), are often called Siegert states [876]. Poles lying in the lower half k-plane and far away from the real positive k-axis contribute to the smooth "background" or "non-resonant" scattering. The distribution of poles in the complex k-plane has been discussed in detail in a few cases, most notably by Nussenzveig [700] for scattering by a square well potential.

We now consider an isolated pole in the S-matrix which lies in the lower half k-plane close to the positive real k-axis. We show that this pole gives rise to

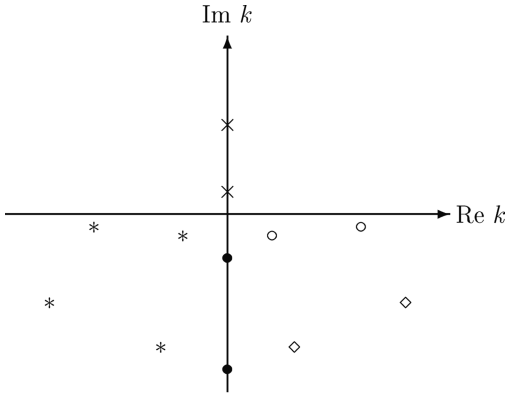

Fig. 1.1 Distribution of S-matrix poles in the complex k-plane. $\times$, poles corresponding to bound states; $\circ$, poles corresponding to resonances; $\diamond$, poles corresponding to background scattering; $*$, conjugate poles required by the symmetry and unitarity relations; $\bullet$, poles corresponding to virtual states

resonance scattering at the nearby real energy. We assume that the pole occurs at the complex energy

$$E = E_r - \tfrac{1}{2}\mathrm{i}\Gamma\,, \tag{1.102}$$

where E_r, the resonance position, and Γ, the resonance width, are both real positive numbers and where from (1.3) we remember that $E = \frac{1}{2}k^2$. Now from the unitarity relation (1.97) we see that corresponding to this pole there is a zero in the S-matrix at a complex energy in the upper half k-plane given by

$$E = E_r + \tfrac{1}{2}\mathrm{i}\Gamma\,. \tag{1.103}$$

For energies E on the real axis in the neighbourhood of this pole, the S-matrix can be written in the following form which is both unitary and explicitly contains the pole and zero:

$$S_\ell(k) = \exp\left[2\mathrm{i}\delta_\ell^0(k)\right]\frac{E - E_r - \frac{1}{2}\mathrm{i}\Gamma}{E - E_r + \frac{1}{2}\mathrm{i}\Gamma}\,. \tag{1.104}$$

The quantity $\delta_\ell^0(k)$ in this equation is called the "background" or "non-resonant" phase shift. Provided that the energy E_r is not close to threshold, $E = 0$, nor to another resonance then the background phase shift is slowly varying with energy. Comparing (1.99) and (1.104) we obtain the following expression for the phase shift:

$$\delta_\ell(k) = \delta_\ell^0(k) + \delta_\ell^r(k)\,, \tag{1.105}$$

where we have written

$$\delta_\ell^r(k) = \tan^{-1}\frac{\frac{1}{2}\Gamma}{E_r - E}\,. \tag{1.106}$$

The quantity $\delta_\ell^r(k)$ is called the "resonant" phase shift which we see from (1.106) increases through π radians as the energy E increases from well below to well above the resonance position E_r. It is also clear from (1.106) that the rapidity of this increase is inversely proportional to Γ, the resonance width.

If the background phase shift $\delta_\ell^0(k)$ is zero then we obtain from (1.30) and (1.106) the following expression for the partial wave cross section:

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\frac{\frac{1}{4}\Gamma^2}{(E - E_r)^2 + \frac{1}{4}\Gamma^2}\,. \tag{1.107}$$

This expression is called the Breit–Wigner one-level resonance formula first derived to describe nuclear resonance reactions [135]. We see that at the energy $E = E_r$ the

partial wave cross section σ_ℓ reaches its maximum value $4\pi(2\ell+1)/k^2$ allowed by unitarity and decreases to zero well below and well above this energy.

If the background phase shift $\delta_\ell^0(k)$ is non-zero then the partial wave cross section can be written as

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell(k) = \frac{4\pi}{k^2}(2\ell+1)\frac{(\epsilon+q)^2}{1+\epsilon^2}\sin^2\delta_\ell^0(k)\,, \tag{1.108}$$

where ϵ is the reduced energy

$$\epsilon = \frac{E-E_r}{\frac{1}{2}\Gamma} \tag{1.109}$$

and q is the resonance shape parameter or line profile index

$$q = -\cot\delta_\ell^0(k)\,. \tag{1.110}$$

The line profile index was introduced by Fano [301] to describe resonant atomic photoionization processes. It follows from (1.108) that the partial wave cross section is zero when $\epsilon = -q$ and achieves its unitarity limit $4\pi(2\ell+1)/k^2$ when $\epsilon = q^{-1}$. In Fig. 1.2 we illustrate the total phase shift $\delta_\ell(k)$ and the partial wave cross section σ_ℓ for s-wave scattering for four different values of the background phase shift,

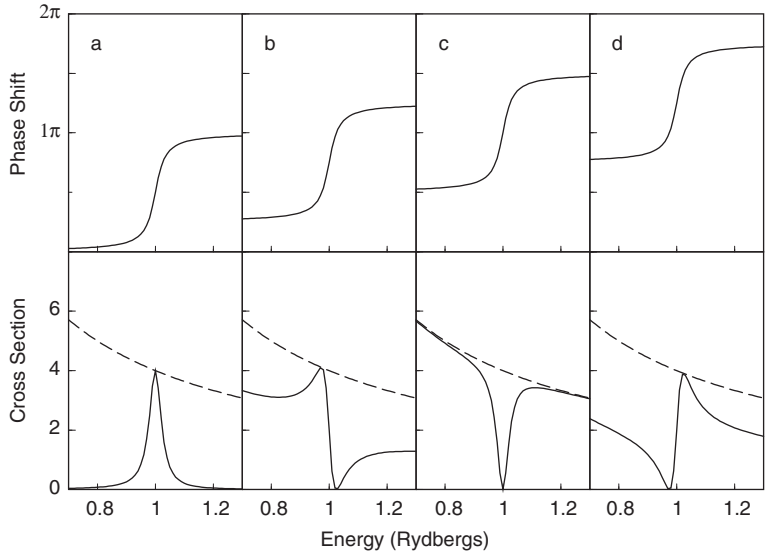

Fig. 1.2 The total phase shift $\delta_\ell(k)$ and the partial wave cross section σ_ℓ for s-wave resonance scattering with $k_r^2 = 2E_r = 1.0$ and $\Gamma = 0.05$ for four different values of the background phase shift. Case (**a**), $\delta_0^0(k) = 0$ giving $q = \infty$; case (**b**), $\delta_0^0(k) = \pi/4$ giving $q = -1$; case (**c**), $\delta_0^0(k) = \pi/2$ giving $q = 0$; case (**d**), $\delta_0^0(k) = 3\pi/4$ giving $q = 1$. The *cross section* is given in πa_0^2 units and the *dashed lines* are the s-wave unitarity limit $4k^{-2}$

which we assume is energy independent. Case (a) with $q = \infty$ corresponds to a standard Breit–Wigner resonance given by (1.107), where the non-resonant background scattering is zero. Case (c) with $q = 0$ corresponds to a window resonance where the background scattering has its maximum value allowed by unitarity. Finally, cases (b) and (d) are intermediate cases where the resonance shapes are asymmetric.

When several resonance poles lie in the lower half k-plane and close to the positive real k-axis their effects on the cross section may overlap. In the case of n resonances we must replace (1.104) by

$$S_\ell(k) = \exp\left[2\mathrm{i}\delta_\ell^0(k)\right] \prod_{j=1}^{n} \frac{E - E_j - \frac{1}{2}\mathrm{i}\Gamma_j}{E - E_j + \frac{1}{2}\mathrm{i}\Gamma_j}\,, \tag{1.111}$$

where the position of the jth pole is $E = E_j - \frac{1}{2}\mathrm{i}\Gamma_j$. The total phase shift is then given by

$$\delta_\ell(k) = \delta_\ell^0(k) + \sum_{j=1}^{n} \tan^{-1} \frac{\frac{1}{2}\Gamma_j}{E_j - E}\,. \tag{1.112}$$

In this case the total phase shift increases through $n\pi$ radians as the energy increases from below all the resonances to above all the resonances, provided that the non-resonant phase shift $\delta_\ell^0(k)$ is slowly varying over this range. The corresponding cross section will achieve its unitarity limit n times where the total phase shift goes through an half odd integral multiple of π radians and will have n zeros where it goes through an integral multiple of π radians.

1.4 Effective Range Theory

In this section we consider the analytic behaviour of the phase shift and the scattering amplitude in the neighbourhood of threshold energy. We show that there is a close relationship between the low-energy scattering amplitude and the bound-state spectrum at negative energies. We consider first the analytic properties for short-range potentials, where the potential vanishes faster than any inverse power of the distance. We then extend our discussion to the situation where the potential behaves asymptotically as r^{-s} where $s \geq 2$, which is relevant for low-energy electron scattering by neutral atoms. Finally, we consider scattering by a Coulomb potential which is relevant to electron–ion scattering.

1.4.1 Short-Range Potentials

We commence by considering the solution of the radial Schrödinger equation (1.8) where we assume that the potential $U(r)$ satisfies the condition

$$U(r) = 0, \quad r \geq a\,, \tag{1.113}$$

for some finite radius a. It follows from (1.9) and (1.15) that the solution which is regular at the origin satisfies the asymptotic boundary condition

$$u_\ell(r) = s_\ell(kr) + c_\ell(kr)K_\ell(k), \quad r \geq a. \tag{1.114}$$

In order to determine the analytic properties of the K-matrix $K_\ell(k)$ we relate it to the R-matrix $R_\ell(E)$ which we introduce in Sect. 4.1 and which is defined on the boundary $r = a$ by

$$u_\ell(a) = R_\ell(E)\left(a\frac{\mathrm{d}u_\ell}{\mathrm{d}r} - bu_\ell\right)_{r=a}, \tag{1.115}$$

where b is an arbitrary constant. Substituting (1.114) for $u_\ell(r)$ into (1.115) then yields

$$[K_\ell(k)]^{-1} = \frac{c_\ell(ka) - R_\ell(E)[kac'_\ell(ka) - bc_\ell(ka)]}{-s_\ell(ka) + R_\ell(E)[kas'_\ell(ka) - bs_\ell(ka)]}, \tag{1.116}$$

where $s'_\ell(kr)$ and $c'_\ell(kr)$ are the derivatives of $s_\ell(kr)$ and $c_\ell(kr)$ with respect to the argument kr.

The analytic properties of the R-matrix are discussed in Sect. 4.1, where we show that it is a real meromorphic function of the energy with simple poles only on the real energy axis. The analytic properties of the functions $s_\ell(kr)$ and $c_\ell(kr)$ and their derivatives are related to those of the spherical Bessel and Neumann functions $j_\ell(kr)$ and $n_\ell(kr)$ defined by (1.10) and (1.11). These functions are discussed in Appendix C.2, where we show that they can be expanded about $z = 0$ as follows:

$$\begin{aligned} j_\ell(z) &= [(2\ell+1)!!]^{-1}z^\ell + O(z^{\ell+2}), \\ n_\ell(z) &= -[(2\ell-1)!!]z^{-\ell-1} + O(z^{-\ell+1}). \end{aligned} \tag{1.117}$$

Hence $k^{-\ell-1}s_\ell(kr)$, $k^{-\ell}s'_\ell(kr)$, $k^\ell c_\ell(kr)$ and $k^{\ell+1}c'_\ell(kr)$ are entire functions of k^2, that is they are analytic functions of k^2 for fixed r. It follows from (1.116) that the M-matrix, which is defined by the equation

$$M_\ell(k^2) = k^{2\ell+1}\,[K_\ell(k)]^{-1}, \tag{1.118}$$

is a real analytic function of k^2 which can be expanded in a power series in k^2 about $k^2 = 0$. It is also useful to express the T-matrix element defined by (1.26) in terms of $M_\ell(k^2)$. We find using (1.118) that

$$T_\ell(k) = \frac{2\mathrm{i}k^{2\ell+1}}{M_\ell(k^2) - \mathrm{i}k^{2\ell+1}}. \tag{1.119}$$

We will see in Chap. 3 that this result generalizes in a straightforward way to multichannel scattering. Also, remembering from (1.15) that $K_\ell(k) = \tan\delta_\ell(k)$, it follows that we can expand $k^{2\ell+1}\cot\delta_\ell(k)$ about zero energy in the form

$$k^{2\ell+1}\cot\delta_\ell(k) = -\frac{1}{a_\ell} + \frac{1}{2}r_{e\ell}k^2 + O(k^4)\,, \tag{1.120}$$

where a_ℓ is called the "scattering length" and $r_{e\ell}$ is called the "effective range". This "effective range expansion" or "Blatt–Jackson expansion" was first derived by Blatt and Jackson [115] and by Bethe [104].

We can obtain a simple physical picture of the s-wave scattering length a_0 in terms of the zero-energy wave function. If we adopt the following normalization of the s-wave reduced radial wave function

$$u_0(r) \underset{r\to\infty}{\sim} \sin kr + \cos kr\tan\delta_0(k), \quad r \geq a\,, \tag{1.121}$$

then in the limit as the energy tends to zero, we find using (1.120) that

$$\lim_{k\to 0} u_0(r) = k(r - a_0), \quad r \geq a\,. \tag{1.122}$$

It follows that the s-wave scattering length a_0 is the intercept of the extrapolation of the asymptote of the zero-energy s-wave reduced radial wave function with the r-axis.

As an example of the relationship between the s-wave scattering length and the zero-energy wave function we consider the solution of (1.8) for a square-well potential. We consider the solution of the equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - U(r) + k^2\right)u(r) = 0\,, \tag{1.123}$$

where the range $r = a$ of the potential $U(r)$ is taken to equal 1 so that

$$\begin{aligned} U(r) &= -A, \quad r < 1, \\ U(r) &= 0, \quad r \geq 1\,, \end{aligned} \tag{1.124}$$

and the energy $E = \frac{1}{2}k^2 = 0$. Also the sign of the potential strength A is chosen so that it is positive for attractive potentials and negative for repulsive potentials.

We show in Fig. 1.3, three examples of the solution $u(r)$ of (1.123) and (1.124) for three different potential strengths. The first example, shown in Fig. 1.3a, corresponds to a repulsive potential where the scattering length $a_0 = 0.5$, the second example, shown in Fig. 1.3b, corresponds to a weak attractive potential which does not support a bound state where $a_0 = -1$ and the third example, shown in Fig. 1.3c, corresponds to a stronger attractive potential which supports one bound state where $a_0 = 2$.

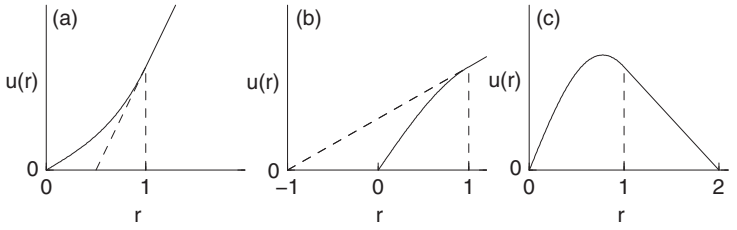

Fig. 1.3 The s-wave zero-energy reduced radial wave function $u(r)$, represented by the *full lines*, showing the scattering length a_0 for three square-well potentials with unit radius: (**a**) a repulsive potential with potential strength $A = -3.667$, giving $a_0 = 0.5$; (**b**) a weak attractive potential with potential strength $A = 1.359$, giving $a_0 = -1$; (**c**) a stronger attractive potential with potential strength $A = 4.116$, giving $a_0 = 2$. Also, represented by the *dashed lines* in (**a**) and (**b**) are the extrapolations of $u(r)$ for $r \geq 1$ back to its intercept $r = a_0$ with the r-axis

The relationship between the s-wave scattering length a_0 and the potential strength A is obtained by solving (1.123) and (1.124) subject to the condition that the solution $u(r)$ and its derivative are continuous on the boundary $r = 1$. We can show that the relationship for repulsive potentials $A < 0$ is

$$a_0 = 1 - \alpha^{-1} \tanh \alpha, \quad \text{where } \alpha^2 = -A\,, \tag{1.125}$$

and the relationship for attractive potentials $A > 0$ is

$$a_0 = 1 - \alpha^{-1} \tan \alpha, \quad \text{where } \alpha^2 = A\,. \tag{1.126}$$

The dependence of the scattering length a_0 on the potential strength A, given by (1.125) and (1.126), is shown in Fig. 1.4 for A in the range $-30 < A < 30$, where we have indicated by crosses on this figure the (A, a_0) values corresponding to the three solutions shown in Fig. 1.3. For an infinitely strong repulsive potential, or hard-core potential, where $A = -\infty$, the scattering length equals the range of the potential, which is unity in this example. As the potential strength increases towards attractive values, the scattering length decreases and passes through zero when $A = 0$, becoming infinitely negative when the asymptote of the solution $u(r)$ is parallel to the r-axis. We see from (1.126) that this occurs when $A = (\pi/2)^2$. A further increase in the potential strength leads to a large positive scattering length, resulting in the support of a bound state. The scattering length again decreases with increasing attraction, becoming infinitely negative again when $A = (3\pi/2)^2$. We see from (1.126) that this process is repeated with each new branch, corresponding to a new state becoming bound, occurring when $A = [(2n+1)\pi/2]^2$, $n = 0, 1, 2, \ldots$. Finally we observe that the same general picture occurs for square-well potentials of arbitrary range a, the strength of the potential where the asymptotes of the solution $u(r)$ are parallel to the r-axis then being given by $A = [(2n+1)\pi/(2a)]^2$, $n = 0, 1, 2, \ldots$.

We now discuss the relationship between the scattering length and effective range and the low-energy behaviour of the S-matrix, T-matrix and cross section. Provided

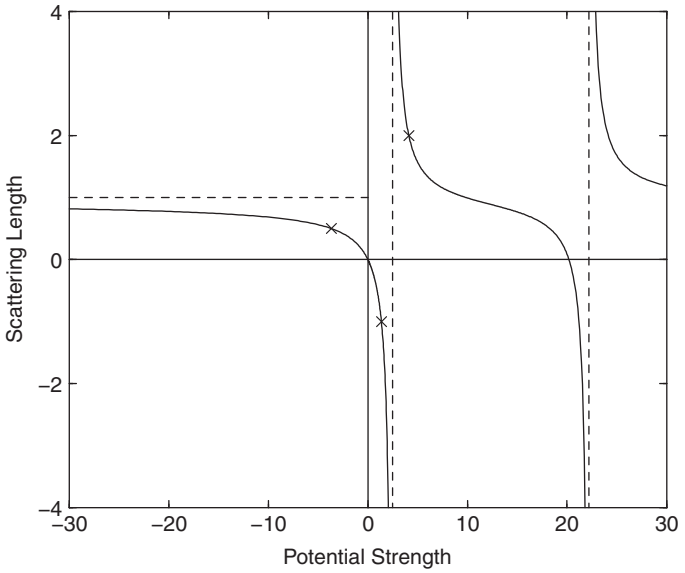

Fig. 1.4 The dependence of the scattering length a_0 on the potential strength A for a square-well potential with unit range. The scattering length and potential strength corresponding to Fig. 1.3a–c is marked by *crosses* on this figure

that the p-wave scattering length a_1 is non-singular then the s-wave partial wave cross section dominates low-energy scattering. It follows from (1.30) and (1.120) that the low-energy s-wave cross section

$$\sigma_0 = \frac{4\pi}{k^2}\sin^2\delta_0(k) = \frac{4\pi}{k^2}\frac{1}{1+\cot^2\delta_0(k)} = \frac{4\pi a_0^2}{k^2a_0^2 + (1-\frac{1}{2}r_{e0}k^2a_0)^2}\,. \quad (1.127)$$

The zero-energy cross section is thus $4\pi a_0^2$. Also, when an s-wave bound state occurs at zero energy then the scattering length and hence the cross section is infinite. We now determine the behaviour of the cross section when an s-wave bound state occurs close to zero energy. It follows from (1.15) and (1.26) that

$$T_\ell(k) = S_\ell(k) - 1 = \frac{2\mathrm{i}}{\cot\delta_\ell(k) - \mathrm{i}}\,. \quad (1.128)$$

Hence a pole in the S- and T-matrices occurs when $\cot\delta_\ell(k) = \mathrm{i}$. However, we saw in Sect. 1.3, see Fig. 1.1, that a bound-state pole in the S-matrix and hence in the T-matrix must lie on the imaginary k-axis, so that

$$k_b = \mathrm{i}\kappa_b\,, \quad (1.129)$$

where κ_b is real and positive. Combining (1.128) and (1.129) we obtain the following condition

$$k_b \cot \delta_0(k_b) = -\kappa_b \,, \tag{1.130}$$

for an s-wave bound state. By comparing this equation with the effective range expansion (1.120) we find that the scattering length is related to the position of the pole in the S- and T-matrices by

$$\kappa_b = a_0^{-1} \,, \tag{1.131}$$

where we have retained only the first term on the right-hand side of (1.120). Substituting this result into (1.127) gives the following expression for the low-energy s-wave cross section:

$$\sigma_0 = \frac{4\pi}{k^2 + \kappa_b^2} \,. \tag{1.132}$$

As we have already remarked, the s-wave cross section is infinite at zero energy when the bound-state pole occurs at zero energy. Also, since this cross section is independent of the sign of κ_b, it is not possible to distinguish by measuring the cross section alone, whether the pole in Fig. 1.1 corresponds to a bound state with positive κ_b or a virtual state with negative κ_b.

In the case of non-zero partial waves we obtain the following expression for the T-matrix by combining (1.120) and (1.128)

$$T_\ell(k) = \frac{2\mathrm{i}k^{2\ell+1}}{-a_\ell^{-1} + \frac{1}{2} r_{e\ell} k^2 - \mathrm{i}k^{2\ell+1}} \,, \tag{1.133}$$

which can be written in the form

$$T_\ell(k) = \frac{\mathrm{i}\Gamma}{E_r - E - \frac{1}{2}\mathrm{i}\Gamma} \,, \tag{1.134}$$

where the resonance position is given by

$$E_r = \frac{1}{a_\ell r_{e\ell}} \tag{1.135}$$

and the resonance width by

$$\Gamma = -\frac{2}{r_{e\ell}} k^{2\ell+1} \,. \tag{1.136}$$

It follows that the effective range $r_{e\ell}$, corresponding to a low-energy resonance with $l \geq 1$, must be negative and its width energy dependent. This type of resonance is

caused by the repulsive angular momentum barrier $\ell(\ell+1)r^{-2}$ which inhibits its decay.

Finally, we can show that although we have derived the effective range expansion (1.120) for a finite range potential satisfying (1.120), it is valid if the potential falls off as fast as, or faster than, an exponential.

1.4.2 Long-Range Potentials

We now consider modifications that have to be made to the effective range expansion (1.120) when the potential $U(r)$ in the radial Schrödinger equation (1.8) behaves asymptotically as follows:

$$U(r) = \frac{A}{r^s}, \quad r \geq a, \quad s \geq 2\,. \tag{1.137}$$

We can determine the required modifications by considering the first Born approximation for the phase shift given by (1.20), that is by

$$\tan\delta_\ell^B(k) = -k\int_0^\infty U(r)\, j_\ell^2(kr) r^2 \mathrm{d}r\,, \tag{1.138}$$

which is applicable here since the coefficients in the effective range expansion arise from the long-range tail of the potential where it is weak. In the limit as $k \to 0$ we can use the power series expansion (C.33) for the spherical Bessel function $j_\ell(kr)$ in (1.138). It follows that the first term in the expansion of the integral in (1.138) only converges for large r if $s > 2\ell + 3$, which gives rise to the first term in the effective range expansion (1.120). If $s \leq 2\ell + 3$ the integral diverges and the first term in the effective range expansion is no longer defined. In a similar way, the second term in the expansion of the integral in (1.138) only converges for large r if $s > 2\ell + 5$ and consequently if $s \leq 2\ell + 5$ the second term in the effective range expansion is not defined. Summarizing these results for the terms in the effective range expansion (1.120) we obtain

$$\begin{aligned} &\text{scattering length } a_\ell \text{ defined if } s > 2\ell + 3 \\ &\text{effective range } r_{e\ell} \text{ defined if } \quad s > 2\ell + 5\,, \end{aligned} \tag{1.139}$$

and so on for higher terms in the effective range expansion.

An important example of long-range potentials occurs in elastic electron scattering by an atom in a non-degenerate s-wave ground state such as atomic hydrogen or the inert gases. We discuss this polarization potential in detail in Sect. 2.2.2, see (2.19), where we show that $U(r)$ has the asymptotic form

$$U(r) = 2V_p(r) \underset{r\to\infty}{\sim} -\frac{\alpha}{r^4}\,, \tag{1.140}$$

where α is the dipole polarizability. The radial Schrödinger equation (1.8) then becomes

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} + \frac{\alpha}{r^4} + k^2\right) u_\ell(r) = 0, \quad r \geq a\,, \tag{1.141}$$

where a is the radius beyond which the potential achieves its asymptotic form. In order to obtain the threshold behaviour of the phase shift we use the Born approximation (1.138), where we consider the contribution to this integral arising from $r \geq a$. Calling this contribution I_ℓ we obtain, after writing $x = kr$,

$$I_\ell = \frac{\pi\alpha k^2}{2} \int_{ka}^{\infty} J^2_{\ell+\frac{1}{2}}(x) x^{-3} \mathrm{d}x\,, \tag{1.142}$$

where for $\ell \geq 1$, the contribution to the integral from $r < a$ behaves as $k^{2\ell+1}$ for small k and can therefore be neglected compared with I_ℓ as $k \to 0$. Also, for $\ell \geq 1$ the integral in (1.142) converges at its lower limit for all $k \geq 0$. Carrying out this integral we find that

$$k^2 \cot \delta_\ell(k) = \frac{8(\ell+\frac{3}{2})(\ell+\frac{1}{2})(\ell-\frac{1}{2})}{\pi\alpha} + \text{ higher order terms}, \quad \ell \geq 1\,. \tag{1.143}$$

It follows in accord with (1.139) that the scattering length is not defined in the presence of a long-range polarization potential when $\ell \geq 1$.

For s-wave scattering in a long-range polarization potential, the contribution to the integral from $r < a$ dominates (1.142) and hence (1.143) is no longer applicable. In this case O'Malley et al. [704] transformed (1.141) into a modified form of Mathieu's equation. Replacing $s_\ell(kr)$ and $c_\ell(kr)$ in (1.114) by the appropriate regular and irregular solutions of this equation and using the known analytic behaviour of the Mathieu functions they obtained

$$k \cot \delta_0(k) = -\frac{1}{a_0} + \frac{\pi\alpha}{3a_0^2}k + \frac{2\alpha}{3a_0}k^2 \ln\left(\frac{\alpha k^2}{16}\right) + O(k^2), \quad \ell = 0\,. \tag{1.144}$$

This equation differs from (1.120) due to the presence of terms containing k and $k^2 \ln k$. Hence the scattering length a_0 is defined but the effective range is not, in accord with (1.139).

The low-energy behaviour of the total cross section in the presence of a long-range polarization potential can be obtained by substituting the above result into (1.30). We obtain

$$\sigma_{\mathrm{tot}}(k) = 4\pi\left(a_0 + \frac{\pi\alpha}{3}k + \cdots\right)^2, \tag{1.145}$$

where we have omitted higher order terms in k and higher partial wave contributions. It follows that the derivative of the total cross section with respect to energy is infinite at threshold, whereas in the absence of the polarization potential it is finite. Also, if the scattering length a_0 is negative, then the total cross section will decrease from threshold and in the absence of significant contributions from higher terms in the expansion (1.145) will become zero when $k = k_0$ where

$$k_0 = -\frac{3a_0}{\pi\alpha}\,. \tag{1.146}$$

This leads to the Ramsauer minimum which occurs, for example, in the total cross section for low-energy electron scattering from the heavier inert gases Ar, Kr and Xe where the scattering length a_0 is negative. On the other hand, if a_0 is positive, as is the case for electron scattering by He and Ne, there is no low-energy minimum in the cross section.

Levy and Keller [588] have considered the general case of potentials whose behaviour at large distances is given by (1.137). They found that

$$\tan\delta_\ell(k) = \tfrac{1}{2}\pi A k^{s-2}\frac{2^{1-s}\Gamma(s-1)\Gamma(\ell+\frac{3}{2}-\frac{1}{2}s)}{\Gamma^2(\frac{1}{2}s)\Gamma(\ell+\frac{1}{2}+\frac{1}{2}s)}, \quad 2 < s < 2\ell+3 \tag{1.147}$$

and

$$\tan\delta_\ell(k) = -\frac{Ak^{2\ell+1}\ln k}{[(2\ell+1)!!]^2}, \quad s = 2\ell+3\,. \tag{1.148}$$

By considering the contribution from higher angular momenta we find that the total threshold cross section is finite if $s > 2$ while the differential cross section is finite if $s > 3$.

Another long-range potential of interest is a dipole potential which falls off asymptotically as r^{-2} and is less singular than r^{-2} at the origin. This occurs in many applications, for example, in the scattering of electrons by polar molecules or by hydrogen atoms in degenerate excited states. The radial Schrödinger equation then has the asymptotic form

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - \frac{A}{r^2} + k^2\right) u_\ell(r) = 0, \quad r \geq a\,. \tag{1.149}$$

This equation has analytic solutions which we can obtain by combining the r^{-2} terms as follows:

$$\lambda(\lambda+1) = \ell(\ell+1) + A\,, \tag{1.150}$$

which has the solution

$$\lambda = -\tfrac{1}{2} \pm \tfrac{1}{2}\left[(2\ell+1)^2 + 4A\right]^{1/2}\,. \tag{1.151}$$

Using this definition, (1.149) reduces to the standard form

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\lambda(\lambda+1)}{r^2} + k^2\right) u_\ell(r) = 0, \quad r \geq a\,. \tag{1.152}$$

where λ is in general a non-integral quantity. In analogy with (1.10) and (1.11) we can define two linearly independent solutions of (1.152) by

$$s_\lambda(kr) = krj_\lambda(kr) \underset{r\to\infty}{\sim} \sin(kr - \tfrac{1}{2}\lambda\pi) \tag{1.153}$$

and

$$c_\lambda(kr) = -krn_\lambda(kr) \underset{r\to\infty}{\sim} \cos(kr - \tfrac{1}{2}\lambda\pi)\,, \tag{1.154}$$

where it is convenient to choose the upper positive sign in (1.151) so that $\lambda \to \ell$ in the limit $A \to 0$.

The solution of the radial Schrödinger equation, corresponding to a dipole potential $U(r)$, which is regular at the origin can be written in analogy with (1.114) by

$$u_\ell(r) = s_\lambda(kr) + c_\lambda(kr)K_\lambda(k), \quad r \geq a\,, \tag{1.155}$$

which defines the K-matrix $K_\lambda(k)$. We can relate the physical K-matrix $K_\ell(k)$, defined by (1.9) and (1.15), to $K_\lambda(k)$, defined by (1.155). We find that

$$K_\ell(k) = \frac{\sin\tau + \cos\tau\, K_\lambda(k)}{\cos\tau - \sin\tau\, K_\lambda(k)}\,, \tag{1.156}$$

where

$$\tau = \tfrac{1}{2}\pi(\ell - \lambda)\,. \tag{1.157}$$

It follows that when $A = 0$ then $\ell = \lambda$ and $K_\ell(k) = K_\lambda(k)$.

In order to determine the analytic behaviour of $K_\lambda(k)$ in the neighbourhood of threshold energy, we proceed as in the derivation of (1.118) by relating $K_\lambda(k)$ to the R-matrix on the boundary $r = a$. We substitute $u_\ell(r)$, given by (1.155), into (1.115) which yields (1.116) with ℓ replaced everywhere by λ. We then use the analytic properties of the functions $s_\lambda(kr)$ and $c_\lambda(kr)$ and their derivatives, which are related to those of the spherical Bessel and Neumann functions $j_\lambda(kr)$ and $n_\lambda(kr)$ through (1.10) and (1.11). In this way we can show that the M-matrix, which is defined by the equation

$$M_\lambda(k^2) = k^{2\lambda+1}\,[K_\lambda(k)]^{-1}\,, \tag{1.158}$$

is an analytic function of k^2 in the neighbourhood of threshold which is a real analytic function when λ is real. We can also express the T-matrix $T_\ell(k)$ defined by (1.26) in terms of the M-matrix, using (1.156) and (1.158). We find that

$$T_\ell(k) = \frac{2\mathrm{i}\mathrm{e}^{2\mathrm{i}\tau}k^{2\lambda+1}}{M_\lambda(k^2) - \mathrm{i}k^{2\lambda+1}} + \mathrm{e}^{2\mathrm{i}\tau} - 1\,, \tag{1.159}$$

which reduces to (1.119) in the limit $A \to 0$ so that $\tau \to 0$.

An important feature of scattering by a dipole potential occurs for strong attractive potentials where

$$A < -\tfrac{1}{4}(2\ell+1)^2\,. \tag{1.160}$$

In this case, the argument of the square root in (1.151) becomes negative and λ, which then becomes complex, can be written as

$$\lambda = -\tfrac{1}{2} + \mathrm{i}\,\mathrm{Im}\,\lambda\,, \tag{1.161}$$

where $\mathrm{Im}\,\lambda$ can be positive or negative. The factor $k^{2\lambda+1}$ in (1.159) can then be written as

$$k^{2\lambda+1} = k^{2\mathrm{i}\,\mathrm{Im}\lambda} = \exp(2\mathrm{i}\,\mathrm{Im}\,\lambda\ln k)\,. \tag{1.162}$$

We see immediately that this gives rise to an infinite number of oscillations in the partial wave cross section as the collision energy tends to zero. Also, if we consider complex values of k defined by

$$k = |k|\mathrm{e}^{\mathrm{i}\phi}\,, \tag{1.163}$$

then the denominator $D_\lambda(k) = M_\lambda(k^2) - \mathrm{i}k^{2\lambda+1}$ in (1.159) can be written as

$$D_\lambda(k) = M_\lambda(k^2) - \exp(-2\phi\mathrm{Im}\,\lambda)\exp\left[2\mathrm{i}\left(\mathrm{Im}\,\lambda\ln|k| + \frac{\pi}{4}\right)\right]. \tag{1.164}$$

It follows that $D_\lambda(k)$ has zeros along lines in the complex k-plane given by

$$|M_\lambda(k^2)| = \exp(-2\phi\mathrm{Im}\,\lambda)\,, \tag{1.165}$$

which gives

$$\phi = -\frac{\ln|M_\lambda(k^2)|}{2\,\mathrm{Im}\,\lambda}\,. \tag{1.166}$$

Also as $|k| \to 0$ then the quantity

$$\theta = \mathrm{Im}\,\lambda\ln|k| + \tfrac{1}{4}\pi \tag{1.167}$$

in (1.164) will increase or decrease through π radians an infinite number of times. Hence the T-matrix has an infinite number of poles converging to the origin along two lines in the now infinite sheeted complex k-plane, where these two lines correspond to the positive and negative values of $\mathrm{Im}\,\lambda$ in (1.167). These lines of poles correspond to bound states, resonances or virtual states depending on the value of ϕ and whether they lie on the physical sheet of the complex k-plane.

We will see when we discuss multichannel effective range theory in Sect. 3.3 that the oscillatory behaviour of the cross section above threshold and the infinite series of bound states below threshold apply in certain circumstances both to electron scattering by polar molecules and by atomic hydrogen in degenerate excited states. The above discussion provides an introduction to these more complicated and realistic situations.

We conclude this section by considering the properties of the total and momentum transfer cross sections at finite energies in the presence of a long-range r^{-2} potential. For high angular momentum ℓ the radial wave function in (1.155) is accurately represented by the first term $s_\lambda(kr)$. Hence the corresponding phase shift is given by

$$\delta_\ell = \tfrac{1}{2}\pi(\ell - \lambda)\,. \tag{1.168}$$

For large ℓ we find by expanding the square root in (1.151) and choosing the upper sign in this equation that

$$\delta_\ell \underset{\ell\to\infty}{\sim} -\frac{\pi A}{2(2\ell+1)} + O(\ell^{-3})\,. \tag{1.169}$$

The total cross section, defined by (1.30), then becomes

$$\sigma_{\rm tot} = \sigma_1 + \sigma_2, \tag{1.170}$$

where

$$\sigma_1 = \frac{4\pi}{k^2}\sum_{\ell=0}^{L}(2\ell+1)\sin^2\delta_\ell \tag{1.171}$$

and

$$\sigma_2 = \frac{4\pi}{k^2}\sum_{\ell=L+1}^{\infty}(2\ell+1)\sin^2\delta_\ell \approx \frac{\pi^3 A^2}{k^2}\sum_{\ell=L+1}^{\infty}\frac{1}{(2\ell+1)}\,. \tag{1.172}$$

In (1.171) and (1.172) L is the value of ℓ where the phase shift δ_ℓ can be accurately represented by the first term on the right-hand side of (1.169). It follows that σ_2, and hence the total cross section $\sigma_{\rm tot}$, diverges logarithmically with ℓ. Also the scattering amplitude, defined by (1.29), and hence the differential cross section, defined by (1.4), diverge in the forward direction. Since the contribution to the differential cross section in the forward direction arising from the short-range component of the potential $U(r)$ is negligible compared with that arising from the long-range r^{-2} component, the corresponding angular distribution is energy independent. In practice, the divergence in the forward direction is cut off either because of the Debye screening of the dipole potential at large distances if the scattering process occurs

in a plasma or because of the molecular rotational splitting or the fine-structure splitting of the target levels.

Finally, we remark that the momentum transfer cross section defined by (1.6) remains finite in the forward direction. This follows immediately by substituting the asymptotic expansion for the phase shift given by (1.169) into (1.31). This result can also be seen to follow from (1.6), where the factor $(1 - \cos\theta)$ cuts off the divergence in the scattering amplitude in the forward direction.

1.4.3 Coulomb Potential

Finally in this section we consider electron or positron scattering by a positive or negative ion. In this case we consider the solution of the radial Schrödinger equation (1.70), where we assume that the short-range part of the potential $U(r)$ vanishes for $r \geq a$. Hence the total potential reduces in this region to the Coulomb potential alone given by

$$U_c(r) = \frac{2Z_1 Z_2}{r}, \quad r \geq a\,, \tag{1.173}$$

where Z_1 and Z_2 are the charge numbers corresponding to the incident particle and the ion, respectively, and where we assume that the ion has infinite mass. The solution of (1.70) which is regular at the origin can be written as follows:

$$u_\ell(r) = F_\ell(\eta, kr) + G_\ell(\eta, kr)K_\ell(k), \quad r \geq a\,, \tag{1.174}$$

where $F_\ell(\eta, kr)$ and $G_\ell(\eta, kr)$ are the regular and irregular Coulomb wave functions, defined by (1.58) and (1.59), respectively, η is defined by (1.42) and $K_\ell(k)$ is the K-matrix.

In order to derive an effective range expansion we commence from (1.115) which defines the R-matrix $R_\ell(E)$ in terms of the radial wave function $u_\ell(r)$ and its derivative $\mathrm{d}u_\ell(r)/\mathrm{d}r$ on the boundary $r = a$ of the internal region. We then substitute $u_\ell(r)$, defined by (1.174), into (1.115) and set the arbitrary constant $b = 0$. After re-arranging terms and using the Wronskian relation $F'_\ell G_\ell - G'_\ell F_\ell = 1$ we obtain

$$[K_\ell(k)]^{-1} = -\frac{G_\ell}{F_\ell} + \frac{1}{F'_\ell F_\ell} + \frac{1}{\sqrt{\rho}F'_\ell}\left[R_\ell(E) - \rho^{-1}\frac{F_\ell}{F'_\ell}\right]\frac{1}{F'_\ell\sqrt{\rho}}\,, \tag{1.175}$$

where $\rho = ka$ and F_ℓ, G_ℓ and F'_ℓ and G'_ℓ are defined by

$$\begin{aligned} F_\ell &= F_\ell(\eta, ka), \qquad G_\ell = G_\ell(\eta, ka), \\ F'_\ell &= \frac{1}{k}\left.\frac{\mathrm{d}F_\ell(\eta, kr)}{\mathrm{d}r}\right|_{r=a}, \quad G'_\ell = \frac{1}{k}\left.\frac{\mathrm{d}G_\ell(\eta, kr)}{\mathrm{d}r}\right|_{r=a}. \end{aligned} \tag{1.176}$$

It follows from (1.175) that the analytic behaviour of $K_\ell(k)$ in the complex energy plane can be obtained in terms of the analytic properties of F_ℓ, G_ℓ, F'_ℓ and $R_\ell(E)$, where we remember that $R_\ell(E)$ is a real meromorphic function of the energy with simple poles only on the real energy axis.

The Coulomb wave functions, which were introduced and discussed in Sect. 1.2, can be written as follows:

$$F_\ell(\eta, kr) = C_\ell(\eta)(kr)^{\ell+1}\Phi_\ell(\eta, kr) \tag{1.177}$$

and

$$G_\ell(\eta, kr) = \frac{(kr)^{-\ell}}{(2\ell+1)C_\ell(\eta)} \times \left[\Psi_\ell(\eta, kr) + (kr)^{2\ell+1}\, p_\ell(\eta)\left(\ln(2kr) + \frac{q_\ell(\eta)}{p_\ell(\eta)}\right)\Phi_\ell(\eta, kr)\right], \tag{1.178}$$

where $\Phi_\ell(\eta, kr)$ and $\Psi_\ell(\eta, kr)$ are entire functions of k^2 and $C_\ell(\eta)$ is defined by (1.60) and (1.61). Also in (1.178)

$$p_\ell(\eta) = 2\eta(2\ell+1)\frac{C_\ell^2(\eta)}{C_0^2(\eta)}\,, \tag{1.179}$$

and

$$\frac{q_\ell(\eta)}{p_\ell(\eta)} = f(\eta)\,, \tag{1.180}$$

is a rational function of η^2 which tends to a constant as $|\eta^2| \to \infty$. Finally

$$f(\eta) = \frac{1}{2}[\psi(\mathrm{i}\eta) + \psi(-\mathrm{i}\eta)]\,, \tag{1.181}$$

where $\psi(z)$ is the Psi (digamma) function which is defined in terms of the gamma function $\Gamma(z)$ by

$$\psi(z) = \frac{\mathrm{d}\Gamma(z)}{\mathrm{d}z}\,. \tag{1.182}$$

Using these properties of the Coulomb wave functions, it then follows from (1.175) that the M-matrix, defined by

$$M_\ell(k^2) = k^{2\ell+1}[(2\ell+1)!!]^2 C_\ell^2(\eta)[K_\ell(k)]^{-1} + h_\ell(\eta)\,, \tag{1.183}$$

is a real analytic function of k^2, where

$$h_\ell(\eta) = k^{2\ell+1}[(2\ell+1)!!]^2\left[2\eta\tau\frac{C_\ell^2(\eta)}{C_0^2(\eta)} - \mathrm{i}C_\ell^2(\eta)\right] \tag{1.184}$$

and

$$\tau = \ln k + f(\eta) + \frac{\mathrm{i}\pi}{\mathrm{e}^{2\pi\eta} - 1}\,. \tag{1.185}$$

Hence $M_\ell(k^2)$ can be expanded in a power series in k^2 giving the following effective range expansion for a Coulomb potential

$$k^{2\ell+1}[(2\ell+1)!!]^2 C_\ell^2(\eta)\cot\delta_\ell(k) + h_\ell(\eta) = -\frac{1}{a_\ell} + \frac{1}{2}r_{e\ell}k^2 + O(k^4)\,, \tag{1.186}$$

where we have expressed $K_\ell(k)$ in (1.183) in terms of the phase shift $\delta_\ell(k)$ using (1.15) and where a_ℓ is the scattering length and $r_{e\ell}$ is the effective range. Equation (1.186) was first derived for s-wave scattering by Bethe [104]. It is also convenient to rewrite this effective range expansion for the T-matrix, defined by (1.26), in terms of the M-matrix. We find that

$$T = \frac{2\mathrm{i}k^{2\ell+1}[(2\ell+1)!!]^2 C_\ell^2(\eta)}{M_\ell(k^2) - k^{2\ell+1}[(2\ell+1)!!]^2 p_\ell(\eta)\tau(2\ell+1)^{-1}}\,. \tag{1.187}$$

In the limit $\eta \to 0$, corresponding to short-range potentials, we can show that

$$[(2\ell+1)!!]^2 C_\ell^2(\eta) \to 1, \quad (2\ell+1)!!]^2 p_\ell(\eta)\tau \to \mathrm{i}, \quad h_\ell(\eta) \to 0\,. \tag{1.188}$$

Hence (1.186) reduces to the effective range expansion (1.120) and (1.187) reduces to (1.119). We will consider the generalization of (1.187) to multichannel scattering by a Coulomb potential in Sect. 3.3.3.

When the Coulomb potential is attractive, corresponding to electron scattering by positive ions or positron scattering by negative ions, we can relate the energies of the bound states to the positive energy scattering phase shift. We have shown in Sect. 1.3 that the poles of the S-matrix, and hence the T-matrix, which lie on the imaginary axis in the complex k-plane, correspond to bound states. It follows from (1.187) that these poles occur when

$$M_\ell(k^2) = k^{2\ell+1}[(2\ell+1)!!]^2 p_\ell(\eta)\tau(2\ell+1)^{-1}\,. \tag{1.189}$$

The branches of the function τ in (1.189) for negative energies, corresponding to positive imaginary k, give rise to an infinite number of solutions of (1.189) converging onto zero energy. These solutions correspond to the Rydberg series of bound states. The relationship between positive and negative energies is obtained using Stirling's series for the Psi functions in the definition of $f(\eta)$ given by (1.181). We find that

$$\tau = \ln z + \frac{\mathrm{i}\pi}{\mathrm{e}^{2\pi\eta} - 1} + \chi(k^2), \quad k^2 > 0 \tag{1.190}$$

and

$$\tau = \ln z + \pi \cot\left(\frac{\pi z}{\kappa}\right) + \chi(k^2), \quad k^2 < 0\,, \tag{1.191}$$

where $k = \mathrm{i}\kappa$ below threshold and $z = -Z_1 Z_2$. Also in (1.190) and (1.191) $\chi(k^2)$ is a real analytic function of k^2 which has the following representation in the neighbourhood of $k^2 = 0$:

$$\chi(k^2) = \sum_{r=1}^{\infty} \frac{B_r}{2r(2r-1)^2} \left(\frac{k}{z}\right)^{2r}, \tag{1.192}$$

where B_r are Bernoulli numbers. Hence, using (1.191), we see from (1.189) that the bound-state energies are given by the solutions of

$$M_\ell(k^2) = k^{2\ell+1}[(2\ell+1)!!]^2 2\eta \frac{C_\ell^2(\eta)}{C_0^2(\eta)} \left[\ln z + \pi \cot\left(\frac{\pi z}{\kappa_b}\right) + \chi(k^2)\right], \tag{1.193}$$

where we have substituted for $p_\ell(\eta)$ in (1.189) using (1.179). Since $M_\ell(k^2)$, $k^{2\ell+1}[(2\ell+1)!!]^2 2\eta C_\ell^2(\eta)/C_0^2(\eta)$ and $\chi(k^2)$ in (1.193) are analytic functions of energy then $\cot(\pi z/\kappa_b)$, where $k^2 = -\kappa_b^2$ are the bound-state energy solutions of (1.193), can be fitted by an analytic function of energy and extrapolated to positive energies.

At positive energies it follows from (1.183) that

$$\cot\delta_\ell(k) = \frac{M_\ell(k^2) - h_\ell(\eta)}{k^{2\ell+1}[(2\ell+1)!!]^2 C_\ell^2(\eta)}\,, \tag{1.194}$$

where we have rewritten $[K_\ell(k)]^{-1}$ in (1.183) as $\cot\delta_\ell(k)$. We then substitute for $M_\ell(k^2)$, defined by (1.193), and $h_\ell(\eta)$, defined by (1.184), in (1.194) yielding

$$\cot\delta_\ell(k) = \frac{2\eta}{C_0^2(\eta)} \left[\ln z + \pi \cot\left(\frac{\pi z}{k}\right) + \chi(k^2)\right] - \frac{2\eta\tau}{C_0^2(\eta)} + \mathrm{i}\,. \tag{1.195}$$

Finally, we substitute for τ, defined by (1.190), in (1.195) yielding the final result

$$\frac{\cot\delta_\ell(k)}{\mathrm{e}^{2\pi\eta} - 1} = \cot\left(\frac{\pi z}{\kappa_b}\right). \tag{1.196}$$

We interpret this equation by extrapolating $\cot(\pi z/\kappa_b)$ on the right-hand side, which is defined at the bound-state energies $k^2 = -\kappa_b^2$, to positive energies, where it is defined in terms of the phase shift $\delta_\ell(k)$, given by the expression on the left-hand side.

We can rewrite (1.196) in a more convenient form by introducing effective quantum numbers ν_n and associated quantum defects μ_n of the bound states by the equation

$$-\kappa_b^2 = -\frac{z^2}{\nu_n^2} = -\frac{z^2}{(n-\mu_n)^2}, \quad n = \ell+1,\ \ell+2,\ \ldots, \tag{1.197}$$

where μ_n is a slowly varying function of energy which is zero when the non-Coulombic part of the potential vanishes. Substituting (1.197) into (1.196) gives

$$\frac{\cot\delta_\ell(k)}{1-\mathrm{e}^{2\pi\eta}} = \cot[\pi\mu(k^2)]\,, \tag{1.198}$$

where $\mu(k^2)$ is an analytic function of energy which assumes the values μ_n at the bound-state energies. For small positive energies the factor $\exp(2\pi\eta)$ is negligibly small and (1.198) then reduces to

$$\delta_\ell(k) = \pi\mu(k^2)\,. \tag{1.199}$$

This result enables bound-state energies, which are often accurately known from spectroscopic observations, to be extrapolated to positive energies to yield electron–ion scattering phase shifts and hence the corresponding partial wave cross sections.

Equations (1.198) and (1.199) were first derived by Seaton [851, 852] and are the basis of single-channel quantum defect theory. The foundations of modern quantum defect theory were laid by Hartree [443], who considered bound-state solutions of the Schrödinger equation (1.8). Further interest in this theory was stimulated by the work of Bates and Damgaard [75], whose Coulomb approximation provided a powerful method for the computation of bound–bound oscillator strengths for simple atomic systems. An interest in quantum defect theory also arose in solid state physics discussed by Kuhn and van Vleck [551], which led to developments in the mathematical theory described in a review article by Ham [440]. In recent years quantum defect theory has been extended to multichannel scattering by Seaton [854] and co-workers, and a comprehensive review of the theory and applications has been written by Seaton [859]. We review multichannel quantum defect theory in Sect. 3.3.4.

We show in Fig. 1.5 an application of single-channel quantum defect theory to e^-–He^+ $^1\mathrm{S}^\mathrm{e}$ and $^3\mathrm{S}^\mathrm{e}$ scattering carried out by Seaton [855]. In this work

$$Y(k^2) = A^{-1}(k^2,\ell)\tan[\pi\mu(k^2)]\,, \tag{1.200}$$

rather than $\cot[\pi\mu(k^2)]$, was used in the extrapolation of the quantum defects, where $A(k^2,\ell)$ is an analytic function of energy defined by

$$A(k^2,\ell) = \prod_{s=0}^{\ell}\left(1+\frac{s^2k^2}{z^2}\right), \tag{1.201}$$

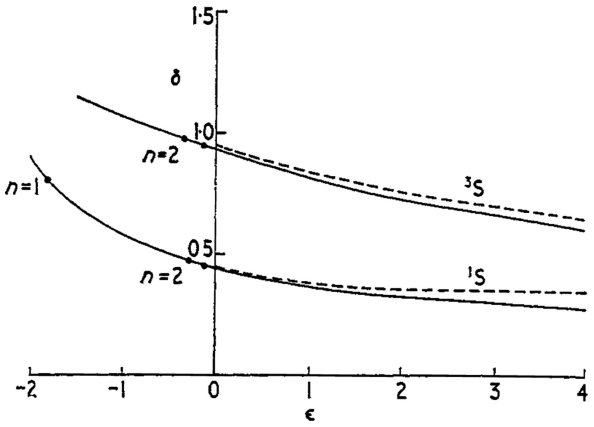

Fig. 1.5 Phase shifts δ in radians versus energy ϵ in Rydbergs for e^-–He^+ $^1S^e$ and $^3S^e$ scattering. *Full lines*, extrapolations using single-channel quantum defect theory; *broken lines*, polarized orbital calculations by Sloan [880]. The *points* at negative energies correspond to the experimental bound-state energies of He (Fig. 1 from [855])

which in the present application equals unity, since the angular momentum ℓ of the scattered electron is zero. A least-squares fit was then made to the bound-state data and the positive energy phase shifts determined using a re-arrangement of (1.198) for $\tan\delta_\ell(k)$. We see in Fig. 1.5 that the phase shifts obtained by extrapolation from the experimental bound-state energies are in excellent agreement with polarized orbital phase shift calculations by Sloan [880] close to threshold and remain good up to quite high energies. This agreement provides experimental confirmation of the accuracy of the theoretical phase shift calculations at low energies.

An important feature of the phase shift for electron scattering from positive ions, which is apparent from Fig. 1.5, is that it does not tend to $n\pi$ radians at threshold energy. This is in contrast to the phase shift for scattering by neutral targets which tends to a multiple of π radians as the scattering energy tends to zero. This is because the attractive Coulomb potential $U_c(r)$ pulls the scattered electron into a region where the short-range part of the potential $U(r)$ in (1.70) is effective, even for non-zero angular momenta. This effect is the same as that which causes the quantum defect μ_n in (1.197) to be non-zero at threshold.

When the Coulomb potential $U_c(r)$ is repulsive, which is the situation when electrons scatter from negative ions or positrons scatter from positive ions, the scattered electron or positron is kept away from the target at low energies and the phase shift vanishes rapidly as the energy tends to zero. In this case $\eta = Z_1 Z_2/k$ is positive and large. It follows from (1.61) that the quantity $[C_0(\eta)]^2$, which in this context is called the Coulomb penetration factor, is given to a good approximation by

$$[C_0(\eta)]^2 \approx 2\pi\eta \exp(-2\pi\eta)\,. \tag{1.202}$$

The factor $\exp(-2\pi\eta)$ in (1.202) is called the Gamow factor [361]. It then follows from (1.186) and (1.202) that

$$\delta_\ell(k) \underset{k\to 0}{\sim} \exp\left(-\frac{2\pi Z_1 Z_2}{k}\right), \quad Z_1 Z_2 > 0\,, \tag{1.203}$$

which applies for all angular momenta. It is clear that the Gamow factor strongly inhibits scattering at low energies when the Coulomb potential is repulsive.

The case when the potential $U(r)$ in (1.70) has a long-range component, falling off asymptotically as r^{-s} where $s > 1$, in addition to the Coulomb potential $U_c(r)$, has been considered by Berger and Spruch [91]. When the Coulomb potential is attractive the threshold behaviour of the phase shift is left unmodified, since the electron is pulled into the region where the short-range component of $U(r)$ is dominant. However, when the Coulomb potential is repulsive, the tail of $U(r)$ is important at low energies since this is the only part of the potential seen by the scattered electron. An important example of this situation is when the leading non-Coulombic component of the potential is due to the polarization of the ion so that $s = 4$. In this case we find that

$$\tan\delta_\ell(k) = \frac{1}{15}\alpha^2 k^5\,, \tag{1.204}$$

where α is the dipole polarizability. Clearly this contribution to the phase shift will dominate the contribution arising from (1.203) at sufficiently low energies.

1.5 Variational Principles

Variational principles were introduced in scattering theory by Hulthén [480, 481], Tamm [909–911], Schwinger [841] and Kohn [542]. In this section we derive Kohn variational principles for the partial wave phase shift and for the S-matrix which have been widely used in electron scattering. This section thus provides an introduction to multichannel variational principles discussed in Sects. 2.4 and 5.2. For specialized treatments of variational principles in scattering see, for example, Demkov [259], Moiseiwitsch [656] and Nesbet [678].

We commence by considering the radial Schrödinger equation (1.8) or (1.70), which we rewrite as

$$L_\ell u_\ell(r) = 0\,, \tag{1.205}$$

which defines the operator L_ℓ. We consider a solution $u_\ell(r)$ of (1.205) satisfying the boundary conditions

$$\begin{aligned} u_\ell(0) &\underset{r\to 0}{\sim} nr^{\ell+1}, \\ u_\ell(r) &\underset{r\to\infty}{\sim} \sin(\theta_\ell + \tau) + \cos(\theta_\ell + \tau)\tan(\delta_\ell - \tau)\,, \end{aligned} \tag{1.206}$$

where n is a normalization factor and where in the case of a long-range Coulomb potential

$$\theta_\ell = kr - \tfrac{1}{2}\ell\pi - \eta\ln 2kr + \sigma_\ell\,, \tag{1.207}$$

with η defined by (1.42) and σ_ℓ defined by (1.62). Also in (1.71) τ is a fixed constant chosen so that $0 \leq \tau \leq \pi$. We note that the solution defined by the boundary conditions (1.206) differs only by a normalization factor $\cos\delta_\ell/\cos(\delta_\ell - \tau)$ from the solution defined by the boundary conditions given by (1.71).

We now consider the functional

$$I_\ell[u_\ell^t] = \int_0^\infty u_\ell^t(r) L_\ell u_\ell^t(r) \mathrm{d}r \,, \tag{1.208}$$

where $u_\ell^t(r)$ is a trial function satisfying the same boundary conditions (1.206) as $u_\ell(r)$ with the phase shift δ_ℓ replaced by a trial phase shift δ_ℓ^t. It is clear from (1.205) and (1.208) that $I_\ell[u_\ell] = 0$. We then find using Green's theorem that

$$\int_0^\infty [u_\ell(r) L_\ell u_\ell^t(r) - u_\ell^t(r) L_\ell u_\ell(r)] \mathrm{d}r = \left[u_\ell \frac{\mathrm{d}u_\ell^t}{\mathrm{d}r} - u_\ell^t \frac{\mathrm{d}u_\ell}{\mathrm{d}r} \right]_0^\infty . \tag{1.209}$$

It follows using the boundary conditions satisfied by u_ℓ and u_ℓ^t that

$$I_\ell[u_\ell^t] - I_\ell[\Delta u_\ell] = k[\tan(\delta_\ell - \tau) - \tan(\delta_\ell^t - \tau)] \,, \tag{1.210}$$

where we have written

$$\Delta u_\ell(r) = u_\ell^t(r) - u_\ell(r) \,. \tag{1.211}$$

Relation (1.210) was first obtained by Kato [525] and is referred to as the Kato identity. If the trial function $u_\ell^t(r)$ is sufficiently close to the exact solution $u_\ell(r)$ then the functional $I_\ell[\Delta u_\ell]$, which is second order of smallness, can be neglected. Equation (1.210) can then be written as

$$\delta[I_\ell + k \tan(\delta_\ell - \tau)] = 0 \,, \tag{1.212}$$

where

$$\delta I_\ell = I_\ell[u_\ell^t] - I_\ell[u_\ell] = I_\ell[u_\ell^t] \tag{1.213}$$

is the change in I_ℓ under the variation $\delta u_\ell^t(r) = u_\ell^t(r) - u_\ell(r)$ and

$$\delta[\tan(\delta_\ell - \tau)] = \tan(\delta_\ell^t - \tau) - \tan(\delta_\ell - \tau) \,. \tag{1.214}$$

Equation (1.212) is known as the Kohn variational principle [542].

The Kohn variational principle (1.212) is clearly satisfied by the exact solution of the differential equation (1.205). It can also be used as the basis for obtaining approximate solutions of (1.205). Thus if we start from a trial function $u_\ell^t(r)$ which depends on n parameters $c_1, c_2, \ldots, c_n$ as well as the phase shift through the quantity λ_ℓ^t defined by

$$\lambda_\ell^t = \tan(\delta_\ell^t - \tau) \,, \tag{1.215}$$

then taking the variation in (1.212) with respect to these $n+1$ parameters yields the equations

$$\frac{\delta I_\ell}{\delta \lambda_\ell^{\mathrm{t}}} = -k \tag{1.216}$$

and

$$\frac{\delta I_\ell}{\delta c_i} = 0, \quad i = 1, \ldots, n\,. \tag{1.217}$$

If the trial function $u_\ell^t(r)$ depends linearly on the parameters $c_1, c_2, \ldots, c_n$ and λ_ℓ^t then (1.216) and (1.217) are a set of $n+1$ linear simultaneous equations which can be solved to yield these parameters. We can then use the variational principle (1.212) to obtain an improved estimate for λ_ℓ which is correct up to terms of second order in the error in the trial function. It is given by

$$[\lambda_\ell] = \lambda_\ell^t + \frac{1}{k} I_\ell[u_\ell^t]\,, \tag{1.218}$$

where the symbol $[\lambda_\ell]$ means that this quantity is the variational estimate of λ_ℓ. The corresponding phase shift, correct up to terms of second order, is then obtained from the variational estimate using the equation

$$[\lambda_\ell] = \tan(\delta_\ell - \tau)\,. \tag{1.219}$$

It follows from the above discussion that different choices of τ in the range $0 \leq \tau \leq \pi$ will yield different variational estimates for the phase shift. Kohn chose $\tau = 0$ so that the trial function satisfied the asymptotic boundary condition

$$u_\ell^t(r) \underset{r\to\infty}{\sim} \sin\theta_\ell + \cos\theta_\ell \tan\delta_\ell^t(k)\,. \tag{1.220}$$

Equation (1.218) then becomes

$$[\tan\delta_\ell] = \tan\delta_\ell^t + \frac{1}{k} I_\ell[u_\ell^t]\,, \tag{1.221}$$

which gives the Kohn variational estimate for $\tan\delta_\ell$ and hence, from (1.15), for the K-matrix. On the other hand Rubinow [800] took $\tau = \pi/2$ so that the trial function satisfied the asymptotic boundary condition

$$u_\ell^t(r) \underset{r\to\infty}{\sim} \cos\theta_\ell + \sin\theta_\ell \cot\delta_\ell^t(k)\,. \tag{1.222}$$

In this case (1.218) yields

$$[\cot\delta_\ell] = \cot\delta_\ell^t - \frac{1}{k} I_\ell[u_\ell^t]\,. \tag{1.223}$$

This approach is often called the Rubinow or inverse Kohn variational principle since it gives a variational estimate for $\cot \delta_\ell = (\tan \delta_\ell)^{-1}$.

It is also often useful to adopt the S-matrix form of the Kohn variational principle. In this case, the solution of (1.205) is chosen to satisfy the asymptotic boundary condition

$$u_\ell(r) \underset{r\to\infty}{\sim} \exp(-\mathrm{i}\theta_\ell) - \exp(\mathrm{i}\theta_\ell) S_\ell(k)\,, \tag{1.224}$$

where the S-matrix $S_\ell(k)$ is defined in terms of the phase shift $\delta_\ell(k)$ by (1.14). We also introduce a trial function $u_\ell^t(r)$ satisfying the asymptotic boundary condition

$$u_\ell^t(r) \underset{r\to\infty}{\sim} \exp(-\mathrm{i}\theta_\ell) - \exp(\mathrm{i}\theta_\ell) S_\ell^t(k)\,. \tag{1.225}$$

As before we consider the variation

$$\delta I_\ell = I_\ell[u_\ell^t] - I_\ell[u_\ell]\,, \tag{1.226}$$

which can be simplified using the boundary conditions satisfied by $u_\ell(r)$ and $u_\ell^t(r)$. Neglecting terms of second order in $\Delta u_\ell(r) = u_\ell^t(r) - u_\ell(r)$ we obtain the S-matrix form of the Kohn variational principle

$$\delta[I_\ell + 2\mathrm{i}k S_\ell] = 0\,, \tag{1.227}$$

where we have written

$$\delta S_\ell = S_\ell^t - S_\ell\,. \tag{1.228}$$

Again if the trial function $u_\ell^t(r)$ depends linearly on n parameters $c_1, c_2, \ldots, c_n$ as well as on the S-matrix S_ℓ^t, then taking the variation in (1.227) with respect to these $n+1$ parameters yields the $n+1$ coupled linear simultaneous equations

$$\frac{\delta I_\ell}{\delta S_\ell^t} = -2\mathrm{i}k \tag{1.229}$$

and

$$\frac{\delta I_\ell}{\delta c_i} = 0, \quad i = 1, \ldots, n\,. \tag{1.230}$$

Equations (1.229) and (1.230) can be solved to yield these $n+1$ parameters. The variational principle (1.227) can then be used to obtain an improved estimate for λ_ℓ which is correct up to terms of second order in the error in the trial function. We find that

$$[S_\ell] = S_\ell^t + \frac{1}{2\mathrm{i}k} I_\ell[u_\ell^t]\,, \tag{1.231}$$

which can be used instead of the Kohn variational estimate for $\tan\delta_\ell$ given by (1.221) or the inverse Kohn variational estimate for $\cot\delta_\ell$ given by (1.223).

In concluding this discussion of variational principles in potential scattering we stress that they are not extremum principles but are only stationary principles. Consequently the variational estimate can lead to misleading results if poor trial functions are used. Indeed, it was shown by Schwartz [838, 839] that anomalous singularities can arise in $[\tan\delta_\ell]$ and in $[\cot\delta_\ell]$ which can invalidate the variational estimate in these cases if care is not taken, even if the number n of trial functions is large. A detailed discussion of these anomalous singularities and methods for avoiding them has been given, for example by Nesbet [675, 676, 678], Burke and Joachain [171] and Cooper et al. [229] and will not be considered further here. However, we remark that the R-matrix method, discussed in Chap. 4 and in later chapters, provides a variational procedure for solving (1.205) which enables phase shifts and S-matrices to be obtained which do not have these singularities.

1.6 Relativistic Scattering: The Dirac Equation

We conclude this chapter on potential scattering by considering relativistic scattering of an electron by a spherically symmetric potential. This situation occurs for relativistic electron scattering energies or for electron collisions with heavy atoms and ions. The wave equation which must then be solved is the time-independent Dirac equation, which takes into account both the spin and the relativistic behaviour of the scattered electron. We consider first the separation of the Dirac equation in spherical polar coordinates which yields two coupled first-order differential equations satisfied by the radial functions describing the motion of the scattered electron. We then derive expressions for the phase shifts, scattering matrix and cross sections in terms of the asymptotic solution of these coupled equations.

The time-independent Dirac equation describing the motion of an electron in a potential $V(\mathbf{r})$ is (see [110, 171, 263, 411]),

$$[\mathrm{c}\boldsymbol{\alpha}\cdot\mathbf{p}+\beta'\mathrm{c}^2+V(\mathbf{r})]\psi(\mathbf{x})=E\psi(\mathbf{x})\,, \tag{1.232}$$

in atomic units, where c is the velocity of light in vacuum, $\mathbf{x}\equiv(\mathbf{r},\sigma)$ represents the space and spin coordinates of the scattered electron and $\mathbf{p}=-\mathrm{i}\nabla$ is the electron momentum operator. Also in (1.232), $\beta'=\beta-I_4$ and $\boldsymbol{\alpha}$ and β are the 4×4 Dirac matrices defined by

$$\boldsymbol{\alpha}=\begin{pmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{pmatrix},\quad \beta=\begin{pmatrix}I_2 & 0\\ 0 & -I_2\end{pmatrix}, \tag{1.233}$$

where the components of $\boldsymbol{\sigma}$, σ_x, σ_y and σ_z, are 2×2 Pauli spin matrices [723] defined by

$$\sigma_x=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad \sigma_y=\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix},\quad \sigma_z=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, \tag{1.234}$$

and I_2 and I_4 are 2×2 and 4×4 unit matrices, respectively. Finally, the choice of β' in (1.232) is made so that the energy E in this equation does not include the electron rest mass and hence reduces in the non-relativistic limit to the energy E in (1.1).

We consider the solution of (1.232) for the case where the potential $V(\mathbf{r})$ is spherically symmetric and hence depends only on the radial variable r and not on the angular variables. We then separate the angular variables in (1.232) from the radial variable using the identity

$$\begin{aligned}\boldsymbol{\alpha}\cdot\mathbf{p} &= \alpha_r p_r + \mathrm{i}r^{-1}\alpha_r(\boldsymbol{\Sigma}\cdot\mathbf{L}+I_4)\\ &= \alpha_r p_r + \mathrm{i}r^{-1}\alpha_r\beta K\,,\end{aligned} \tag{1.235}$$

where the radial momentum operator p_r and the radial velocity operator α_r are defined by

$$p_r = -\mathrm{i}\frac{1}{r}\frac{\partial}{\partial r}r, \quad \alpha_r = r^{-1}\boldsymbol{\alpha}\cdot\mathbf{r}\,, \tag{1.236}$$

and where the operator K is defined by

$$K = \beta(\boldsymbol{\Sigma}\cdot\mathbf{L}+I_4)\,, \tag{1.237}$$

with

$$\boldsymbol{\Sigma} = \begin{pmatrix}\boldsymbol{\sigma} & 0\\ 0 & \boldsymbol{\sigma}\end{pmatrix}, \quad \mathbf{L} = \begin{pmatrix}\boldsymbol{\ell} & 0\\ 0 & \boldsymbol{\ell}\end{pmatrix}. \tag{1.238}$$

The operator K can be shown to commute with the Dirac Hamiltonian and hence its eigenvalues are constants of the motion. Furthermore, since

$$\boldsymbol{\Sigma}\cdot\mathbf{L} = 2\mathbf{S}\cdot\mathbf{L} = \mathbf{J^2}-\mathbf{L^2}-\mathbf{S^2} = \mathbf{J^2}-\mathbf{L^2}-\frac{3}{4}I_4\,, \tag{1.239}$$

then we may rewrite the operator K as

$$K = \beta\left(\mathbf{J^2}-\mathbf{L^2}+\frac{1}{4}I_4\right). \tag{1.240}$$

Also it follows from (1.237) that

$$K^2 = \left(\mathbf{L}+\frac{1}{2}\boldsymbol{\Sigma}\right)^2+\frac{1}{4}I_4\,. \tag{1.241}$$

Since $(\mathbf{L}+\frac{1}{2}\boldsymbol{\Sigma})^2$ is the square of the total angular momentum operator, which has the eigenvalues $j(j+1)$, then the eigenvalues of K^2 are $(j+\frac{1}{2})^2\equiv\kappa^2$ where κ is given by

$$\kappa = \pm 1,\ \pm 2,\ \pm 3,\ \ldots\,. \tag{1.242}$$

Using the above equations, the Dirac equation (1.232) can be written as

$$H\psi(\mathbf{x}) = [\mathrm{c}\alpha_r p_r + \mathrm{i}\mathrm{c}r^{-1}\alpha_r\beta K + \beta'\mathrm{c}^2 + V(r)]\psi(\mathbf{x}) = E\psi(\mathbf{x})\,. \tag{1.243}$$

The solution of (1.243) can be written as a four-component spinor in the form

$$\psi(\mathbf{x}) = \frac{1}{r}\begin{pmatrix} p_\kappa(r)\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) \\ \mathrm{i}q_\kappa(r)\eta_{-\kappa m}(\hat{\mathbf{r}},\sigma)\end{pmatrix}, \tag{1.244}$$

where $p_\kappa(r)$ and $q_\kappa(r)$ are radial functions which depend on κ as described below, and the factor i is introduced so that the radial equations satisfied by $p_\kappa(r)$ and $q_\kappa(r)$, derived below, are real, and hence these functions can be chosen to be real. The spin–angle functions $\eta_{\kappa m}(\hat{\mathbf{r}},\sigma)$ in (1.244) are two-component spinors defined by

$$\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) \equiv \mathcal{Y}_{\ell\frac{1}{2}jm}(\hat{\mathbf{r}},\sigma) = \sum_{m_\ell m_s}(\ell m_\ell \tfrac{1}{2} m_s|jm)Y_{\ell m_\ell}(\theta,\phi)\chi_{\frac{1}{2}m_s}(\sigma)\,, \tag{1.245}$$

where $(\ell m_\ell \frac{1}{2} m_s|jm)$ are Clebsch–Gordan coefficients defined in Appendix A.1, $Y_{\ell m_\ell}(\theta,\phi)$ are spherical harmonics defined in Appendix B.3 and $\chi_{\frac{1}{2}m_s}(\sigma)$ are the usual two-component Pauli spin functions given by

$$\chi_{\frac{1}{2}\frac{1}{2}}(\sigma) = \begin{pmatrix}1\\0\end{pmatrix}, \quad \chi_{\frac{1}{2}-\frac{1}{2}}(\sigma) = \begin{pmatrix}0\\1\end{pmatrix}. \tag{1.246}$$

It then follows from Appendices A and B that the functions $\mathcal{Y}_{\ell\frac{1}{2}jm}(\hat{\mathbf{r}},\sigma)$ defined by (1.245) are simultaneous eigenfunctions of $\mathbf{J}^2$ and $\mathbf{L}^2$ belonging to the eigenvalues $j(j+1)$ and $\ell(\ell+1)$, respectively. Hence

$$\begin{aligned}\left(\mathbf{J}^2 - \mathbf{L}^2 + \tfrac{1}{4}I_2\right)\mathcal{Y}_{\ell\frac{1}{2}jm}(\hat{\mathbf{r}},\sigma) &= \left[j(j+1) - \ell(\ell+1) + \tfrac{1}{4}\right]\mathcal{Y}_{\ell\frac{1}{2}jm}(\hat{\mathbf{r}},\sigma) \\ &= \left[(j+\tfrac{1}{2})^2 - \ell(\ell+1)\right]\mathcal{Y}_{\ell\frac{1}{2}jm}(\hat{\mathbf{r}},\sigma)\,. \end{aligned}\tag{1.247}$$

Using this result and the definition of K given by (1.240) and $\psi(\mathbf{x})$ given by (1.244), we find that

$$K\psi(\mathbf{x}) = -\kappa\psi(\mathbf{x})\,, \tag{1.248}$$

where the eigenvalue κ is then defined by

$$\kappa = \ell(\ell+1) - (j+\tfrac{1}{2})^2\,. \tag{1.249}$$

Hence the eigenvalue κ is related to the orbital and total angular momentum quantum numbers ℓ and j by the equations

$$\begin{aligned}\kappa &= \ell \quad \text{when} \quad j = \ell - \tfrac{1}{2}, \\ \kappa &= -\ell - 1 \quad \text{when} \quad j = \ell + \tfrac{1}{2}\,. \end{aligned}\tag{1.250}$$

Table 1.1 Relationship of κ to the usual spectroscopic notations ℓ and j

κ negative		κ positive	
$\kappa = -1$	$s_{1/2}$	$\kappa = +1$	$p_{1/2}$
$\kappa = -2$	$p_{3/2}$	$\kappa = +2$	$d_{3/2}$
$\kappa = -3$	$d_{5/2}$	$\kappa = +3$	$f_{5/2}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$

This relationship is given explicitly in Table 1.1.

Using the above results for the eigenvalues of the K operator, we can now simplify the Dirac equation defined by (1.243). Substituting (1.244) into (1.243) and using (1.233) and (1.248) we obtain the following coupled equations

$$c\sigma_r(p_r + ir^{-1}\kappa)ir^{-1}q_\kappa(r)\eta_{-\kappa m}(\hat{\mathbf{r}},\sigma) + [V(r) - E]r^{-1}p_\kappa(r)\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) = 0\,, \tag{1.251}$$

and

$$c\sigma_r(p_r - ir^{-1}\kappa)r^{-1}p_\kappa(r)\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) + [-2c^2 + V(r) - E]ir^{-1}q_\kappa(r)\eta_{-\kappa m}(\hat{\mathbf{r}},\sigma) = 0\,. \tag{1.252}$$

These equations can be simplified using the identity

$$\sigma_r\eta_{\pm\kappa m}(\hat{\mathbf{r}},\sigma) = -\eta_{\mp\kappa m}(\hat{\mathbf{r}},\sigma)\,, \tag{1.253}$$

which follows since $\sigma_r = \boldsymbol{\sigma}\cdot\hat{\mathbf{r}}$ is a pseudo-scalar operator and hence it changes the sign of the parity but leaves the total angular momentum and its z-component unaltered. Projecting (1.251) onto the function $\eta_{\kappa m}(\hat{\mathbf{r}},\sigma)$ and (1.252) onto the function $\eta_{-\kappa m}(\hat{\mathbf{r}},\sigma)$ and using (1.236) we find that the time-independent Dirac equation reduces to the following coupled first-order differential equations satisfied by the functions $p_\kappa(r)$ and $q_\kappa(r)$

$$\left(\frac{d}{dr} + \frac{\kappa}{r}\right)p_\kappa(r) - \frac{1}{c}[2c^2 + E - V(r)]q_\kappa(r) = 0 \tag{1.254}$$

and

$$\left(\frac{d}{dr} - \frac{\kappa}{r}\right)q_\kappa(r) + \frac{1}{c}\left[E - V(r)\right]p_\kappa(r) = 0\,, \tag{1.255}$$

which must be solved for each κ. The coupled Eqs. (1.254) and (1.255) take the place of the radial Schrödinger equation (1.8) in non-relativistic theory. We thus see that the Dirac equation for a spherically symmetric potential can be separated without approximation in spherical polar coordinates. We also note from these equations that for scattering energies $E \ll c^2$, the ratio $p_\kappa/q_\kappa \approx c$. Hence p_κ is often referred to as the "large component" and q_κ as the "small component" of the Dirac wave function.

It is instructive at this point to consider the non-relativistic limit of the coupled differential equations (1.254) and (1.255). In this limit

$$|E - V(r)| \ll 2c^2 \,, \tag{1.256}$$

and hence (1.254) can be rewritten as

$$\left(\frac{d}{dr} + \frac{\kappa}{r}\right) p_\kappa(r) - 2cq_\kappa(r) = 0 \,. \tag{1.257}$$

Substituting for $q_\kappa(r)$ from (1.257) into (1.255) then gives

$$\frac{1}{2}\left(\frac{d}{dr} - \frac{\kappa}{r}\right)\left(\frac{d}{dr} + \frac{\kappa}{r}\right) p_\kappa(r) + [E - V(r)]\, p_\kappa(r) = 0 \,, \tag{1.258}$$

which can be rewritten as

$$\left(\frac{d^2}{dr^2} - \frac{\kappa(\kappa+1)}{r^2} - 2V(r) + 2E\right) p_\kappa(r) = 0 \,. \tag{1.259}$$

It follows from (1.250) that $\kappa = \ell$ or $-\ell - 1$, so that in both cases

$$\kappa(\kappa+1) = \ell(\ell+1) \,. \tag{1.260}$$

Also we remember from Sect. 1.1 that $k^2 = 2E$ and the reduced potential $U(r) = 2V(r)$. Hence (1.259) can be written as

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2\right) p_\kappa(r) = 0 \,, \tag{1.261}$$

which is the usual form of the radial Schrödinger equation given by (1.8).

The coupled equations (1.254) and (1.255) can be reduced to Schrödinger form even when (1.256) is not satisfied. This occurs for relativistic electron scattering energies or when the potential $V(r)$ corresponds to electron collisions with heavy target atoms or ions with large nuclear charge number Z. Taking the derivative of (1.254), substituting for dq_κ/dr from (1.255) and eliminating $q_\kappa(r)$ then yields

$$\frac{d^2 p_\kappa}{dr^2} - \frac{A'(r)}{A(r)}\frac{dp_\kappa}{dr} + \left(A(r)B(r) - \frac{A'(r)}{A(r)}\frac{\kappa}{r} - \frac{\kappa(\kappa+1)}{r^2}\right) p_\kappa = 0 \,, \tag{1.262}$$

where we have written

$$\begin{aligned} A(r) &= \frac{1}{c}[2c^2 + E - V(r)] \,, \\ A'(r) &= \frac{dA}{dr} \,, \\ B(r) &= \frac{1}{c}\,[E - V(r)] \,. \end{aligned} \tag{1.263}$$

We then make the substitution

$$p_\kappa(r) = [A(r)]^{1/2}\, \tilde{p}_\kappa(r) \tag{1.264}$$

in (1.262), which gives the following equation for $\tilde{p}_\kappa(r)$:

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\kappa(\kappa+1)}{r^2} - U_\kappa(r) + k_r^2\right)\tilde{p}_\kappa(r) = 0\,, \tag{1.265}$$

where

$$k_r^2 = \frac{1}{\mathrm{c}^2} E(E + 2\mathrm{c}^2) \tag{1.266}$$

and

$$U_\kappa(r) = \frac{2(E+\mathrm{c}^2)V(r)}{\mathrm{c}^2} - \frac{[V(r)]^2}{\mathrm{c}^2} + \frac{\kappa}{r}\frac{A'(r)}{A(r)} + \frac{3}{4}\frac{[A'(r)]^2}{[A(r)]^2} - \frac{1}{2}\frac{A''(r)}{A(r)}\,. \tag{1.267}$$

After substituting for $\kappa(\kappa+1)$ from (1.260), we see that (1.265) has the same form as the non-relativistic Schrödinger equation (1.8). Also, for low-energy electron collisions with light atoms or ions, the terms involving $[V(r)]^2$, $A'(r)$ and $A''(r)$ in (1.267) can be neglected and we obtain

$$A(r) = 2\mathrm{c}, \quad k^2 = 2E, \quad U_\kappa(r) = U(r)\,. \tag{1.268}$$

Hence (1.265) reduces to the non-relativistic Schrödinger equation (1.261) or (1.8) as expected.

However, for relativistic electron scattering energies or for electron collisions with heavy atoms or ions all the terms in the potential $U_\kappa(r)$ given by (1.267) are appreciable. Hence the Dirac equations (1.254) and (1.255) or the equivalent relativistic Schrödinger equation (1.265) gives different results from the non-relativistic Schrödinger equation (1.8) or (1.261) for the same potential $U(r) = 2V(r)$. In particular, the term containing κ in $U_\kappa(r)$ corresponds to a spin–orbit interaction, since from (1.250), $\kappa = \ell$ when $j = \ell - 1/2$ and $\kappa = -\ell - 1$ when $j = \ell + 1/2$. We will see later in this section that this spin–orbit term in $U_\kappa(r)$ gives rise to spin polarization effects in electron collisions with heavy atoms or ions even for low electron scattering energies.

We conclude our discussion of the equivalent relativistic Schrödinger equation (1.265) by noting that although it has the same form as the non-relativistic Schrödinger equation, there are two other fundamental differences. First, the k_r^2 term, defined by (1.266), depends on E^2 as well as upon E and second the relativistic potential $U_\kappa(r)$, defined by (1.267), depends on the energy E as well as upon the radius r. However, for low-energy electron collisions with heavy atoms or ions, where the electron scattering energy $E \ll \mathrm{c}^2$, these differences become insignificant and we obtain in this limit

$$k_r^2 \to k^2 = 2E \tag{1.269}$$

and

$$U_\kappa(r) \to U_{\kappa 0}(r) = 2V(r) - \frac{[V(r)]^2}{c^2} + \frac{\kappa}{r}\frac{A'(r)}{A(r)} + \frac{3}{4}\frac{[A'(r)]^2}{[A(r)]^2} - \frac{1}{2}\frac{A''(r)}{A(r)}\,. \quad (1.270)$$

The corresponding relativistic Schrödinger equation (1.265) then reduces to the standard non-relativistic Schrödinger equation form, as shown in our discussion leading to (1.261), where $k^2 = 2E$ and the potential does not depend on energy. We will see in Sects. 4.6 and 5.5 that this result has important implications for the R-matrix method of solving the Dirac equation describing low-energy electron collisions with heavy atoms or ions.

We now derive expressions for the scattering amplitudes and cross sections by considering the asymptotic form of the solution of the Dirac equation. We commence by noting that it is only necessary to know the "large components" of the Dirac four-component spinor in order to determine the scattering matrix (see, for example, [171]). Thus if the Dirac four-component spinor, given by (1.244), is written in terms of two-component spinors as follows

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}, \quad (1.271)$$

then we need to only consider the two-component spinor ψ_A containing the "large component" $p_\kappa(r)$. In analogy with (1.2), we write the asymptotic form of ψ_A corresponding to a plane wave and outgoing spherical wave as

$$\psi_A(\mathbf{x}) \underset{r\to\infty}{\sim} \chi_{\frac{1}{2}m_s}(\sigma)e^{ikz} + \sum_{m_s'=\pm\frac{1}{2}} \chi_{\frac{1}{2}m_s'}(\sigma) M_{m_s'm_s}(\theta,\phi)\frac{e^{ikr}}{r}, \quad m_s = \pm\tfrac{1}{2}\,, \quad (1.272)$$

where we have assumed that the potential $V(r)$ is short range, vanishing faster than r^{-1} at large distances. Equation (1.272) then defines the scattering matrix $M_{m_s'm_s}(\theta,\phi)$, where the wave number k of the scattered electron is related to the incident electron energy E by (1.266).

In order to determine the scattering matrix, we expand $\psi_A(\mathbf{x})$ in terms of the spin–angle functions $\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) \equiv \mathcal{Y}_{\ell\frac{1}{2}jm}(\hat{\mathbf{r}},\sigma)$ defined by (1.245). We write

$$\psi_A(\mathbf{x}) = \sum_{\ell=0}^{\infty} \sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}} B_{\ell j}(k) r^{-1} p_{\ell j}(r) \mathcal{Y}_{\ell\frac{1}{2}jm_s}(\hat{\mathbf{r}},\sigma)\,, \quad (1.273)$$

where the radial functions $p_{\ell j}(r)$ can be identified with the radial functions $p_\kappa(r)$ which satisfy (1.262). Also from (1.264) and (1.265), and the result that $A(r)$ tends to a constant as $r \to \infty$, it follows that the radial functions $\tilde{p}_\kappa(r)$ and hence the radial functions $p_{\ell j}(r)$ can be chosen to vanish at the origin and to satisfy the asymptotic boundary conditions

$$p_{\ell j}(r) \underset{r\to\infty}{\sim} \sin\left[kr - \tfrac{1}{2}\ell\pi + \delta_{\ell j}(k)\right], \quad j = \ell \pm \tfrac{1}{2}\,. \quad (1.274)$$

In this equation we have introduced the phase shifts $\delta_{\ell j}(k)$ which depend on j as well as on ℓ because of the κ dependence of $U_\kappa(r)$ in (1.265).

The scattering amplitudes and cross sections can be obtained, as in Sect. 1.1, by equating (1.272) with the asymptotic form of (1.273). We first express the incident plane wave term in (1.272) in terms of the spin–angle function $\mathcal{Y}_{\ell\frac{1}{2}jm}$. To achieve this we note from (1.27) that

$$\chi_{\frac{1}{2}m_s}(\sigma)\mathrm{e}^{\mathrm{i}kz} = \chi_{\frac{1}{2}m_s}(\sigma)\sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^\ell j_\ell(kr)P_\ell(\cos\theta)\,. \tag{1.275}$$

Using (B.47) and the inverse of (1.245), which from Appendix A.1 is

$$Y_{\ell m}(\theta,\phi)\chi_{\frac{1}{2}m_s}(\sigma) = \sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}}\left(\ell m_\ell \tfrac{1}{2}m_s|jm_\ell+m_s\right)\mathcal{Y}_{\ell\frac{1}{2}jm_\ell+m_s}(\hat{\mathbf{r}},\sigma)\,, \tag{1.276}$$

enables us to rewrite (1.275) as

$$\chi_{\frac{1}{2}m_s}(\sigma)\mathrm{e}^{\mathrm{i}kz} = \sum_{\ell=0}^{\infty}\sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}}[4\pi(2\ell+1)]^{1/2}\ \mathrm{i}^\ell j_\ell(kr)\left(\ell 0\tfrac{1}{2}m_s|jm_s\right)\mathcal{Y}_{\ell\frac{1}{2}jm_s}(\hat{\mathbf{r}},\sigma)\,. \tag{1.277}$$

The coefficient $B_{\ell j}(k)$ in (1.273) is then determined by equating the ingoing wave terms in (1.273) and (1.277). We find using (1.274) that

$$B_{\ell j}(k) = k^{-1}[4\pi(2\ell+1)]^{1/2}\,\mathrm{i}^\ell\exp[\mathrm{i}\delta_{\ell j}(k)]\left(\ell 0\tfrac{1}{2}m_s|jm_s\right)\,. \tag{1.278}$$

The second term on the right-hand side of (1.272) can now be obtained by subtracting (1.277) from the asymptotic form of (1.273). Calling this term $\psi_{\mathrm{sc}}(\mathbf{x})$ we find that

$$\psi_{\mathrm{sc}}(\mathbf{x}) \underset{r\to\infty}{\sim} \frac{1}{2\mathrm{i}k}\sum_{\ell=0}^{\infty}\sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}}[4\pi(2\ell+1)]^{1/2}\{\exp[2\mathrm{i}\delta_{\ell j}(k)]-1\}\left(\ell 0\tfrac{1}{2}m_s|jm_s\right)$$
$$\times\,\mathcal{Y}_{\ell\frac{1}{2}jm_s}(\hat{\mathbf{r}},\sigma)\frac{\mathrm{e}^{\mathrm{i}kr}}{r}\,. \tag{1.279}$$

The scattering matrix $M_{m_s'm_s}(\theta,\phi)$ is determined by substituting for the spin–angle function $\mathcal{Y}_{\ell\frac{1}{2}jm_s}(\hat{\mathbf{r}},\sigma)$ from (1.245) and comparing with (1.272). We obtain

$$M_{m_s' m_s}(\theta,\phi) = \frac{1}{2ik}\sum_{\ell=0}^{\infty}\sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}} [4\pi(2\ell+1)]^{1/2}\left\{\exp\left[2i\delta_{\ell j}(k)\right]-1\right\}\left(\ell 0\tfrac{1}{2}m_s|jm_s\right) \times \left(\ell m_s - m_s'\tfrac{1}{2}m_s'|jm_s\right) Y_{\ell m_s - m_s'}(\theta,\phi)\,. \tag{1.280}$$

We can write this result as a 2×2 matrix in spin space using the explicit forms for the Clebsch–Gordan coefficients and for the spherical harmonics defined in Appendices A and B, respectively. We find that

$$\mathbf{M}(\theta,\phi) = \begin{pmatrix} f(\theta) & h(\theta)e^{-i\phi} \\ -h(\theta)e^{i\phi} & f(\theta)\end{pmatrix}, \tag{1.281}$$

where the direct scattering amplitude $f(\theta)$ is given by

$$f(\theta) = \frac{1}{2ik}\sum_{\ell=0}^{\infty}\left[(\ell+1)\{\exp[2i\delta_{\ell\ell+\frac{1}{2}}(k)]-1\}+\ell\{\exp[2i\delta_{\ell\ell-\frac{1}{2}}(k)]-1\}\right] \times P_\ell(\cos\theta)\,, \tag{1.282}$$

and the spin-flip scattering amplitude $h(\theta)$ is given by

$$h(\theta) = \frac{1}{2ik}\sum_{\ell=1}^{\infty}\left\{\exp[2i\delta_{\ell\ell+\frac{1}{2}}(k)]-\exp[2i\delta_{\ell\ell-\frac{1}{2}}(k)]\right\}P_\ell^1(\cos\theta)\,. \tag{1.283}$$

We note that if the spin–orbit coupling term in the potential is negligible so that the interaction potential is the same for $j=\ell+\frac{1}{2}$ and $j=\ell-\frac{1}{2}$, then $\delta_{\ell\ell+\frac{1}{2}}(k)=\delta_{\ell\ell-\frac{1}{2}}(k)$. The spin-flip amplitude $h(\theta)$ then vanishes and the direct scattering amplitude $f(\theta)$ reduces to the familiar form given by (1.29) where $\delta_\ell(k)=\delta_{\ell\ell+\frac{1}{2}}(k)=\delta_{\ell\ell-\frac{1}{2}}(k)$.

We can rewrite the scattering matrix (1.281) in terms of the 2×2 unit matrix I_2 and the Pauli spin matrices given in (1.234) as

$$\mathbf{M}(\theta,\phi) = f(\theta)I_2 - ih(\theta)\sin\phi\,\sigma_x + ih(\theta)\cos\phi\,\sigma_y\,. \tag{1.284}$$

This expression can be further simplified if we define the (x,z) plane to be the plane of scattering, with the z-axis being the incident beam direction and the y-axis being normal to this plane. Then $\phi=0$ and we obtain

$$\mathbf{M} = f(\theta)I_2 + ih(\theta)\sigma_y\,. \tag{1.285}$$

If we introduce a unit vector $\hat{\mathbf{n}}$ normal to the scattering plane defined by the incident and scattered electron vectors $\mathbf{k}_i$ and $\mathbf{k}_f$, respectively, so that

$$\hat{\mathbf{n}} = \frac{\mathbf{k}_i \times \mathbf{k}_f}{|\mathbf{k}_i \times \mathbf{k}_f|}\,, \tag{1.286}$$

then the scattering matrix can be written as

$$\mathbf{M} = f(\theta) I_2 + \mathrm{i} h(\theta) \boldsymbol{\sigma} \cdot \hat{\mathbf{n}}\,. \tag{1.287}$$

We note that the scattering matrix $\mathbf{M}$ is a scalar and hence is independent of the particular coordinate system which we have used to obtain it. In fact the expression given by (1.287) is the most general scalar which can be formed in the case of spin $\frac{1}{2}$ particles scattered from a spin zero target under the assumptions of rotational invariance, time-reversal invariance and parity conservation.

Having determined the scattering matrix, we can now calculate the cross sections. The differential cross section for a transition from a state denoted by $(\mathbf{k}, m_s)$ to a state denoted by $(\mathbf{k}', m_s')$ is

$$\frac{\mathrm{d}\sigma_{m_s' m_s}}{\mathrm{d}\Omega} = |\langle \chi_{\frac{1}{2} m_s'} | \mathbf{M} | \chi_{\frac{1}{2} m_s} \rangle|^2 = |M_{m_s' m_s}(\theta, \phi)|^2\,. \tag{1.288}$$

If the spin orientation of the final state is not measured, then the differential cross section for scattering from a pure initial spin state $\chi_{\frac{1}{2} m_s}$ is

$$\begin{aligned} \frac{\mathrm{d}\sigma_{m_s}}{\mathrm{d}\Omega} &= \sum_{m_s' = \pm\frac{1}{2}} |\langle \chi_{\frac{1}{2} m_s'} | \mathbf{M} | \chi_{\frac{1}{2} m_s} \rangle|^2 \\ &= \sum_{m_s' = \pm\frac{1}{2}} \langle \chi_{\frac{1}{2} m_s} | \mathbf{M}^+ | \chi_{\frac{1}{2} m_s'} \rangle \langle \chi_{\frac{1}{2} m_s'} | \mathbf{M} | \chi_{\frac{1}{2} m_s} \rangle \\ &= \langle \chi_{\frac{1}{2} m_s} | \mathbf{M}^+ \mathbf{M} | \chi_{\frac{1}{2} m_s} \rangle\,, \end{aligned} \tag{1.289}$$

where $\mathbf{M}^+$ is the hermitian conjugate of $\mathbf{M}$. Using (1.287) and the identity

$$(\boldsymbol{\sigma} \cdot \mathbf{V}_1)(\boldsymbol{\sigma} \cdot \mathbf{V}_2) = \mathbf{V}_1 \cdot \mathbf{V}_2 + \mathrm{i} \boldsymbol{\sigma} \cdot (\mathbf{V}_1 \times \mathbf{V}_2)\,, \tag{1.290}$$

where $\mathbf{V}_1$ and $\mathbf{V}_2$ are any two vectors, then we find that

$$\begin{aligned} \frac{\mathrm{d}\sigma_{m_s}}{\mathrm{d}\Omega} &= |f(\theta)|^2 + |h(\theta)|^2 + \mathrm{i}[f^*(\theta) h(\theta) - f(\theta) h^*(\theta)] \\ &\quad \times \langle \chi_{\frac{1}{2} m_s} | \boldsymbol{\sigma} \cdot \hat{\mathbf{n}} | \chi_{\frac{1}{2} m_s} \rangle\,. \end{aligned} \tag{1.291}$$

This result can be rewritten as

$$\frac{\mathrm{d}\sigma_{m_s}}{\mathrm{d}\Omega} = \left[|f(\theta)|^2 + |h(\theta)|^2 \right] \left[1 + S(\theta) \mathbf{P}_i \cdot \hat{\mathbf{n}} \right]\,, \tag{1.292}$$

where the real function

$$S(\theta) = \mathrm{i}\frac{f^*(\theta)h(\theta) - f(\theta)h^*(\theta)}{|f(\theta)|^2 + |h(\theta)|^2} \tag{1.293}$$

is called the Sherman function [871] and

$$\mathbf{P}_i = \langle \chi_{\frac{1}{2}m_s} | \boldsymbol{\sigma} | \chi_{\frac{1}{2}m_s} \rangle \tag{1.294}$$

is the initial electron spin polarization vector. Since we are considering a pure initial spin state we have $|\mathbf{P}_i| = 1$. However, (1.292) remains valid for any degree of polarization of the incident electron beam where $0 \leq |\mathbf{P}_i| \leq 1$. Spin and relativistic effects in potential scattering are discussed further by Burke and Joachain [171] and a discussion of polarization phenomena in atomic collisions using a density matrix approach has been given by Blum [119]. We refer to these texts for a more detailed presentation of these phenomena.