

Chapter 2

Time independent scattering matrices and quantization

Much of atomic physics involves scattering processes. Traditionally, scattering involves the continuum states of particles that collide at a relative energy $E > 0$. However, the tools of scattering theory are also useful in treating bound state physics. This chapter describes how scattering theory, and scattering matrices in particular, can be extended to treat the bound ($E < 0$) and continuum ($E > 0$) states of an atomic electron in external electromagnetic fields.

The use of scattering methods to unify bound and continuum physics is not new. Quantum-defect theory was developed, beginning in the 1950s, by Seaton [85, 86, 87, 88] to describe the interaction of an electron with a positive ion. When the interaction of the electron with the positive ion is encapsulated in a scattering (or S) matrix, diverse phenomena such as photoabsorption, autoionization, electron-ion scattering and dielectronic recombination of atoms can be treated within the same framework. The S -matrices introduced in this chapter and used throughout the following chapters rely heavily on the concepts and methods of quantum-defect theory. Because of this, I begin by reviewing the relevant parts of quantum-defect theory. A more thorough introduction to quantum-defect theory can be found in a number of review articles [50, 68].

After the relevant tools of quantum-defect theory have been introduced, S -matrices for the treatment of atoms in external fields emerge with a few simple extensions. The emphasis in this chapter is on the basic definitions and properties of these S -matrices and the physical picture upon which they are built. The details of how the S -matrices can be calculated are delayed until later chapters. One of the central results of this thesis is the derivation of semiclassical approximations for the S -matrices (Ch. 5).

However, unless otherwise noted, all of the formulas and derivations in this chapter will be exact results. It is important to show how exact, quantum mechanical expressions for observables such as the bound state energies and the photoabsorption cross section of atoms in external fields can be derived in terms of the S -matrices. Even before semiclassical approximations are introduced, much physical insight about these nonintegrable systems can be gained by phrasing everything in terms of the S -matrices of this chapter.

Section 1 reviews the needed tools of quantum-defect theory. Section 2 extends the results of quantum-defect theory to include the effects of external fields applied to the atom. Section 3 concludes with a short discussion of the results of Sec. 2.

2.1 Quantum defect theory

Quantum-defect theory (QDT) relies on many of the same concepts as traditional time-independent scattering theory [89]. The most important of these is the asymptotic region. When two particles collide, most of the complicated physics occurs when the particles are very close to each other. Typically, outside this complicated “interaction” region, the physics between the particles simplifies greatly. For instance, when an electron collides with a positive ion, the complicated many body dynamics between the approaching electron and the particles comprising the ion can be neglected when the electron is farther than about 10-20 Bohr radii away. Beyond this distance the long-range electron-ion interaction is simply a spherically symmetric Coulomb potential. The word “asymptotic” reflects the usual case of particles colliding in the continuum where the physics simplifies as the interparticle separation r (also called the fragmentation coordinate) tends off to infinity.

However, it is not necessary for the fragmentation coordinate to approach infinity to use the tools of scattering theory. Rather, scattering theory is useful as long as the physics simplifies in some region of space. It is this perspective that undergirds the success of QDT. That is, QDT uses the fact that when an atomic electron is in a highly excited bound state, it spends most of its time far from the residual ion in a pure Coulomb potential. Thus, in QDT two regions of space are identified. First, at small distances ($r < 10$ a.u.) the electron interacts strongly with the constituents of the ionic core. In this **core**

region the complicated interactions between the electron and the ionic core, including electron-electron repulsion and the Pauli exclusion principle, are important. Second, at large distances ($r > 10$ a.u.) these complicated interactions are unimportant and the electron moves in a pure Coulomb potential. This constitutes the long-range or **matching region**. Here the full solutions of the Schrödinger equation in the core region are matched to a simple form involving Coulomb functions, channel functions and the core region S -matrix $\underline{S}^{\text{core}}$.

2.1.1 Energy normalized Coulomb functions

Before the S -matrix can be defined, the properties of the Coulomb functions must be outlined. As Seaton points out [50], “the whole of quantum-defect theory hinges on a knowledge of their mathematical properties.” The relevant Schrödinger equation for these solutions,

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r} \right) u(r) = Eu(r), \quad (2.1)$$

is that of an electron in an attractive Coulomb potential, where the first derivative with respect to r has been eliminated by the substitution $\psi(r) = u(r)/r$. This second-order linear equation for the Coulomb function $u(r)$ has two linearly independent solutions, which can be chosen in a number of ways. The choice used in this paper (f_{El}^+, f_{El}^-) follows that of [68] and leads to an S -matrix formulation of QDT. For brevity, the explicit energy and l dependence of these functions will often be omitted. These and alternate pairs of linearly independent Coulomb functions have been studied in depth by Seaton [50] and by Greene *et al.* [90, 91].

More details of these Coulomb functions can be found in the above references, but a few of their more important properties are mentioned here. The pair (f^+, f^-) are energy normalized¹ and obey the traveling-wave boundary conditions ($f^{\pm l}(r) = \pm ik(r)f^{\pm}(r)$ in a WKB [24] approximation) typical of scattering theory. However, it should be realized that for negative energies, the traveling wave boundary conditions hold only in the classically allowed regions; these functions diverge exponentially at both

¹ Two solutions are energy normalized if $\langle f_{El}^+ | f_{E'l}^+ \rangle = \delta(E - E')$.

$r \rightarrow \infty$ and $r \rightarrow 0$ when $E < 0$. The Wronskians of these functions,

$$\mathbf{W} [f_l^-, f_l^+] = f_l^- f_l^{+'} - f_l^{-'} f_l^+ = \frac{2i}{\pi}, \quad (2.2)$$

$$\mathbf{W} [f_l^-, f_l^-] = \mathbf{W} [f_l^+, f_l^+] = 0, \quad (2.3)$$

will be used throughout this work. The widely used regular and irregular Coulomb functions² of QDT (f, g) are related to the pair (f^+, f^-) by the relation $f^\pm = (-g \pm if)/\sqrt{2}$. Because this thesis deals primarily with highly excited Rydberg states, their zero-energy form [92],

$$f_l^\pm(r) \longrightarrow \pm i \sqrt{r} H_{2l+1}^{(1,2)}(\sqrt{8r}) \quad (E \rightarrow 0), \quad (2.4)$$

will be useful. Furthermore, when l is “small” and r is “large” the asymptotic forms of the Hankel functions in Eq. (2.4) can be used [93]:

$$H_{2l+1}^{(1,2)}(\sqrt{8r}) \longrightarrow \sqrt{\frac{2}{\pi\sqrt{8r}}} e^{\pm i(\sqrt{8r} - \frac{\pi}{2}(2l+1) - \frac{\pi}{4})} \quad (\text{large } r). \quad (2.5)$$

The semiclassical approximations developed in later chapters will use these approximate forms of the Coulomb functions. Next the other degrees of freedom are addressed.

2.1.2 Channel functions

In quantum-defect theory, all of the information about the ionic core and the spin and angular degrees of freedom of the Rydberg electron is contained in channel functions. These degrees of freedom are typically quantized from the start by expanding the full wavefunction in a discrete set of these channel functions $\phi_i(\Omega)$. Then, in any region, the N linearly independent solutions (labeled by α) of the Schrödinger equation can be written in terms of these channel functions [68] and the multichannel radial wavefunction $F_{i\alpha}(r)$:

$$\psi_\alpha(r, \Omega) = \frac{1}{r} \sum_i \phi_i(\Omega) F_{i\alpha}(r). \quad (2.6)$$

The discrete index i labels the states (or channels) of the ionic core as well as the spin of the Rydberg electron. The continuous coordinate Ω denotes the angular degrees of freedom of the electron. As an

² This pair of Coulomb functions (f, g) leads to an alternative form of QDT that involves a real symmetric K -matrix rather than a complex unitary S -matrix.

example, in the alkali-metal atoms the channel functions are most often just the spherical harmonics $Y_{lm}(\theta, \phi)$. Typically, the channel functions form a complete and orthonormal set. When the expansion of the wavefunction (2.6) is used in the Schrödinger equation and the resulting equation is projected onto the channel functions, the radial wavefunction $\underline{F}(r)$ (now written as a matrix) is found to obey the multichannel radial Schrödinger equation:

$$\frac{1}{2}\underline{F}''(r) + (E - \underline{V})\underline{F}(r) = 0, \quad (2.7)$$

where the effective potential matrix is defined as:

$$V_{ij}(r) = \left\langle \Phi_i \left| \frac{\vec{L}^2}{2r^2} + V(r, \Omega) \right| \Phi_j \right\rangle. \quad (2.8)$$

At a total energy E there are two qualitatively different types of channels: open channels and closed channels. The i th channel is open when a Rydberg electron in that channel can escape to infinity ($E > E_i$ where E_i is the ionization threshold energy for the i th channel). The i th channel is closed when the electron in that channel is bound ($E < E_i$). In multichannel contexts, the energy in the i th channel will always be measured with respect to the ionization threshold energy E_i in that channel, so that quantities such as the Coulomb functions f_i^\pm will be functions of $E - E_i$.

2.1.3 S -matrices in quantum-defect theory

As early practitioners [85, 94] of QDT realized, the most important feature of the energy normalized Coulomb functions is that they allow the results of scattering theory to be continued below threshold to negative energies. The work of QDT begins after the multichannel radial wavefunction $F_{i\alpha}^{\text{core}}(r)$ in the complicated core region has been determined numerically. In the matching region ($r > 10$ a.u.), this function is expressed as,

$$F_{i\alpha}^{\text{core}}(r) = \frac{1}{i\sqrt{2}} [f_i^+(r)P_{i\alpha} - f_i^-(r)Q_{i\alpha}], \quad (2.9)$$

where the matrices \underline{P} and \underline{Q} encapsulate any non-Coulombic physics of the core region. The multichannel S -matrix state (now written as a matrix) $\underline{M}^{\text{core}}(r)$ is simply a linear combination of these numerically

determined solutions,

$$\underline{M}^{\text{core}}(r) = \underline{F}^{\text{core}}(r)\underline{Q}^{-1} = \frac{1}{i\sqrt{2}} [f^+(r)\underline{S}^{\text{core}} - f^-(r)], \quad (2.10)$$

so that the S -matrix is just $\underline{S}^{\text{core}} = \underline{P}\underline{Q}^{-1}$. This specific linear combination of solutions, then, serves to define the core-region S -matrix. As long as the S -matrix state (2.10) is used in the Coulomb region no approximations are made. For the case of hydrogen ($\underline{S}^{\text{core}} = \underline{1}$) the S -matrix state (2.10) reduces to the regular Coulomb function $f_i(r)$. It is important to mention that at this point, only the physical boundary conditions at $r = 0$ have been imposed, while the boundary condition at $r = \infty$ remain unspecified. The key point of QDT is that because the boundary conditions at $r = \infty$ are not imposed, the S -matrix in Eq. (2.10) varies slowly with energy. In most cases it can be regarded as independent of energy over ranges of about 1 eV. All of the rapid energy dependence of physical observables comes from the properties of the energy normalized Coulomb functions. To illustrate how the boundary conditions at $r = \infty$ can be imposed, I now sketch the derivation of the well known modified Rydberg formula [95, 96],

$$E_{nl} = -\frac{1}{2(n - \mu_l)}, \quad (2.11)$$

for the bound levels of an alkali-metal atom. The μ_l are the quantum defects which vanish for the “non-defective” case of hydrogen. The core-region scattering matrix $\underline{S}^{\text{core}}$ for an alkali-metal atom is diagonal in a spherical representation and can be written in terms of these quantum defects:

$$S_{ll'}^{\text{core}} = \delta_{ll'} e^{2\pi i \mu_l}. \quad (2.12)$$

The boundary condition appropriate for bound states is imposed by equating a linear combination of the wavefunction of Eq. (2.10) to a linear combination of wavefunctions that decay exponentially as $r \rightarrow \infty$. The single-channel decaying solution is known as the Whittaker Coulomb function [68] $W_{El}(r)$ and is written in terms of the pair (f^+, f^-) and the Coulomb phase $\beta = \pi(\nu - l)$, where $\nu = 1/\sqrt{-2E}$ is the effective quantum number:

$$W_{El}(r) = \frac{1}{i\sqrt{2}} [f_{El}^-(r)e^{2i\beta} - f_{El}^+(r)] e^{-i\beta}. \quad (2.13)$$

The matching equation between Eq. (2.10) and Eq. (2.13),

$$\underline{M}^{\text{core}}(r) \vec{B}^{\text{core}} = \underline{W}(r) \vec{B}^{\text{LR}}, \quad (2.14)$$

involves undetermined coefficients B_l^{core} and B_l^{LR} . In solving for the vectors of coefficients \vec{B}^{core} and \vec{B}^{LR} , it is found that the all of the boundary conditions (at both $r = 0$ and $r = \infty$) can be satisfied only when the condition,

$$\det(\underline{1} - \underline{S}^{\text{core}} e^{2i\beta(E)}) = 0, \quad (2.15)$$

is true. When $\underline{S}^{\text{core}} = e^{2\pi i\mu}$, as for an alkali-metal atom, the Rydberg formula of Eq. (2.11) emerges as the zeros of this equation. For the purposes of this thesis, I regard Eq. (2.15) as the fundamental equation giving the bound state spectrum of the Rydberg states of an atom. In the following section this equation is generalized to include the effects of a static external electromagnetic field applied to the atom. This analysis of the bound state physics applies when all of the channels are closed. For channels that become open as the energy is increased, outgoing-wave boundary conditions at $r = \infty$ must be applied. The formulas appropriate to this case can be found in the standard QDT literature, but are not provided in this review.

To use the methods of QDT to treat atoms in external electromagnetic fields, a difficulty must be faced. When a static field (magnetic, electric, or a combination of them) is applied to an atom, the long range spherical symmetry is broken. The long range potential of the electron then becomes,

$$V = -\frac{1}{r} + \frac{\rho^2 B^2}{8} + Fz, \quad (2.16)$$

where B is the magnetic field in atomic units ($B(\text{Tesla})/2.35 \times 10^5$) and F is the electric field in the same units ($F(V/m)/5.1423 \times 10^{11}$). It is clear that the external fields destroy the simple long-range Coulomb physics that allowed scattering theory to be used below threshold. The following section shows how this difficulty can be overcome.

2.2 S -matrices for atoms in external fields

As discussed above, the main physical requirement for using scattering theory to treat a problem is that the motion simplifies in some region of space. The key point is that such a region exists for an atomic electron in external electromagnetic fields. While external fields do destroy the long-range spherical symmetry of the Rydberg electron's motion, the electronic physics remains simple at intermediate distances ($10 < r < 100$ a.u.), even in the presence of strong external fields. In this intermediate range of radii, both the effects of the ionic core and of the external fields can be neglected, and again the Rydberg electron evolves in a pure Coulomb potential. For example, in a 6 Tesla magnetic field at a distance of $r = 100$ a.u., the ratio of the diamagnetic energy to the Coulomb energy is approximately 10^{-4} . This feature of an atomic electron in external fields was first recognized by Clark and Taylor [70] and has since been used in most theoretical treatments, both quantum and semiclassical, of these systems. This allows the methods of QDT and scattering theory to be extended to the case of a Hamiltonian that is nonintegrable.

With this in mind, this thesis is founded on the following physical picture. The quantum state of a highly excited atomic electron in the presence of external fields can be pictured as a time-independent scattering process. In this process, the electron scatters multiple times off of the ionic core and the long-range fields (Coulomb and external), each time returning to the simple Coulombic region. All of the information about these scattering events is contained in two scattering matrices: a core region scattering matrix $\underline{S}^{\text{core}}$ and a nontrivial long-range scattering matrix $\underline{S}^{\text{LR}}$. It is important to remember that each S -matrix element is a quantum mechanical amplitude to scatter off the core or long-range region **a single time**. The remainder of this chapter and the next shows how these two S -matrices control the most interesting physics of atoms in external electromagnetic fields.

At this point it is useful to summarize the properties of the three basic regions in which an atomic electron in external fields moves. Figure 2.1 provides a graphical representation of this partitioning of configuration space.

- (1) Core region ($r < 10$ a.u.): Here, complicated interactions such as the electron-electron re-

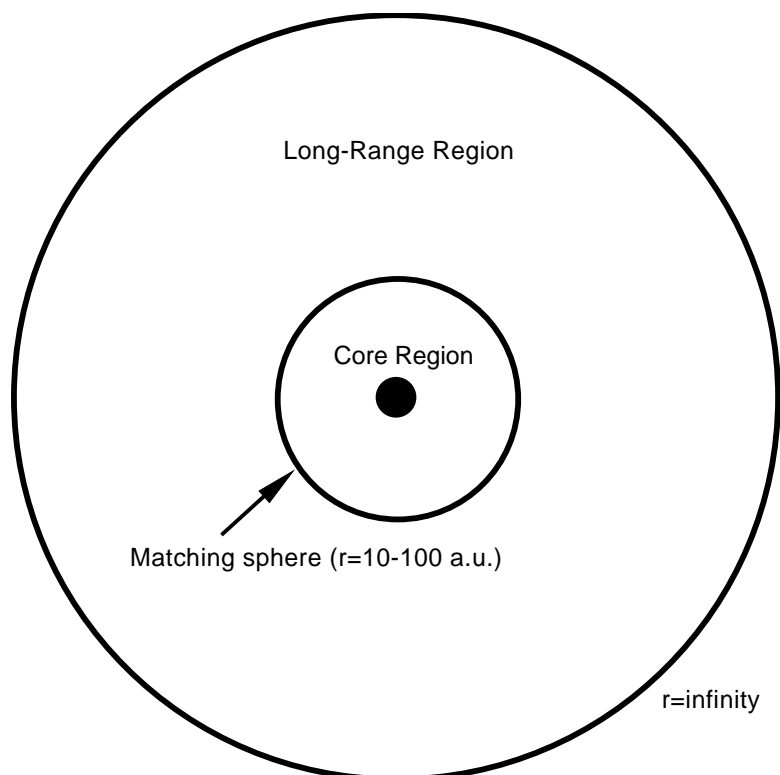


Figure 2.1: The various regions of configuration space in which a Rydberg electron in external electromagnetic fields travels are shown. The core region ($r < 10$ a.u.), matching region ($10 < r < 100$ a.u.), and the long-range region ($r > 100$) are shown as concentric spherical shells. Using the matching region as “home base” the electron scatters either inward off the ionic core (shown as a filled circle at the center), or outward off the long range Coulomb and external field potentials. Each of these scattering processes is encapsulated in a scattering matrix.

pulsion and the Pauli exclusion principle dominate the physics of the Rydberg electron. The external fields can be ignored in this region. As in standard QDT, the physics in this region is encapsulated in an energy independent scattering matrix $\underline{S}^{\text{core}}$.

- (2) Matching region ($10 < r < 100$ a.u.): Here, the Rydberg electron sees only a spherically symmetric Coulomb potential. I call it the matching region because solutions from the core and long-range regions are matched in this region to “ S -matrix states.” Thus, this region functions much like an asymptotic region in traditional scattering theory.
- (3) Long-range region ($100 < r < 10^4$ a.u.): Here, the spherically symmetric Coulomb potential and the external electromagnetic fields compete on an equal footing. Depending on what configuration of external fields are applied, the physics can be integrable (electric and Coulomb field only) or nonintegrable (Coulomb field plus magnetic field or magnetic and electric fields). In either case, the Hamiltonian is not separable in the same coordinate system as the core region, if at all. The physics in this region is encapsulated in a long-range scattering matrix $\underline{S}^{\text{LR}}$.

The exact boundaries between these regions are somewhat flexible and depend on factors such as the total energy, external field strengths and details of the ionic core. The important point is that the physics is qualitatively different in each region.

Although this thesis focuses on bound state physics, one further complication that emerges above threshold deserves mention here. Above the ionization threshold, a fourth region is identified beyond $r = 10^4$. Here, the Coulomb field has become far less important, and the external fields dominate the physics. Again, the details of the physics here are determined by the configuration of external fields that are applied. For the case of an external magnetic field, the electron moves out in decoupled Landau channels along the direction of the magnetic field. For an applied electric field, the electron approaches infinity as an outgoing wave in parabolic coordinates. For the cases of parallel or crossed electric and magnetic fields, the physics is more complicated at infinity, but nonetheless is still approximately integrable.

2.2.1 S -matrix states

Now, using this matching region ($10 < r < 100$ a.u.) like an asymptotic region in traditional scattering theory, scattering matrices for an atomic electron in external fields are introduced. As before, all but the radial degree of freedom will be expanded in a set of channel functions $\Phi_i(\Omega)$. Like both QDT and traditional scattering theory, the S -matrices are defined by writing down particular linear combinations of solutions of the Schrödinger equation, the “ S -matrix states,” in the matching region. However, now there are two S -matrix states. The first, $\underline{M}^{\text{core}}(r)$, is related to the numerically determined solution $\underline{F}^{\text{core}}(r)$ regular at $r = 0$ and determines the core-region S -matrix $\underline{S}^{\text{core}}$. The second, $\underline{M}^{\text{LR}}(r)$, is related to the numerically determined solution $\underline{F}^{\text{LR}}(r)$ having physical boundary conditions at $r = \infty$ and determines the long-range S -matrix $\underline{S}^{\text{LR}}$. In terms of the Coulomb functions and the S -matrices these solutions are:

$$\underline{M}^{\text{core}}(r) = \frac{1}{i\sqrt{2}} [\underline{f}^+(r)\underline{S}^{\text{core}} - \underline{f}^-(r)], \quad (2.17)$$

$$\underline{M}^{\text{LR}}(r) = \frac{1}{i\sqrt{2}} [\underline{f}^-(r)\underline{S}^{\text{LR}} - \underline{f}^+(r)]. \quad (2.18)$$

These forms of the solutions are only valid in the Coulomb matching region ($10 < r < 100$ a.u.). While it may seem that these S -matrix states are “just another set of linearly independent solutions of the Schrödinger equation,” their usefulness will be demonstrated throughout this thesis as they are used to derive a number of important results.

A number of properties of these S -matrices are worth mentioning. By comparing the long-range S -matrix state $\underline{M}^{\text{LR}}(r)$ (2.18) with the Whittaker Coulomb function (2.13) it is seen that the long-range S -matrix with no external fields is simply the diagonal matrix $\underline{S}^{\text{LR}}(E) = e^{2i\beta(E)}$. Thus, unlike the core region S -matrix, the long-range S -matrix depends strongly on the energy. When external fields are applied this strong energy dependence remains, but $\underline{S}^{\text{LR}}(E)$ becomes non-diagonal because of the broken spherical symmetry in the long-range region. As in standard scattering theory, both of these S -matrices are unitary and have finite dimension at a given energy E on the real axis. The dimension of the S -matrices is determined by the number of locally open channels in the matching region. For an alkali-metal atom, this number can be estimated by the maximum classically allowed angular momentum l at a

radius r_0 somewhere in the matching region

$$l_{\max} = \sqrt{2r_0^2 \left(E + \frac{1}{r_0} \right) - \frac{1}{2}}. \quad (2.19)$$

As stated above, the two S -matrices $\underline{S}^{\text{core}}$ and $\underline{S}^{\text{LR}}$ determine the most interesting properties of atomic Rydberg states in external fields. The first such property that I investigate is the bound state energies of the Rydberg electron.

2.2.2 Quantization using S -matrices

The highly excited eigenstates of a nonintegrable Hamiltonian are characterized by global chaos in the classical domain and a lack of good quantum numbers in the quantum domain. Because much of our intuition about quantum eigenstates relies on the existence of good quantum numbers, physical insight about the eigenstates is more difficult to gain in a nonintegrable system. Some of the traditional methods of quantization (separation of variables, perturbation theory) fail completely for nonintegrable systems. Others, such as variational methods, struggle to give any insight about the highly excited states they provide. Because of this, it is desirable to have a method of quantization that is able to give physical insight as well as accurate eigenvalues.

Here I present an alternative to the traditional methods of quantization; one that involves the two scattering matrices $\underline{S}^{\text{core}}$ and $\underline{S}^{\text{LR}}(E)$. The result derived below,

$$\det [\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)] = 0, \quad (2.20)$$

was first suggested by Aymar *et al.* [68], but nothing was known at the time about the details of the long-range S -matrix when external fields are applied to the atom. These details turn out to be very significant as any physical insight contained in Eq. (2.20) must be provided by the S -matrices themselves. A detailed discussion of the physics contained in $\underline{S}^{\text{LR}}$ is delayed until Chs. 4 and 5 where I show how to calculate this S -matrix using accurate quantum calculations and semiclassical approximations. As expected, this condition (2.20) is identical to that of QDT (2.15) with the matrix $e^{2i\beta}$ replaced by the long range scattering matrix $\underline{S}^{\text{LR}}$. Although the derivation of Eq. (2.20) is not difficult, I record the details here as some of the intermediate results will be useful later on.

To derive the quantization condition (2.20), I construct the linear combination of solutions that satisfies the physical boundary conditions at both $r = 0$ and $r = \infty$. Because the S -matrix states $\underline{M}^{\text{core}}(r)$ and $\underline{M}^{\text{LR}}(r)$ in Eqs. (2.17) and (2.18) satisfy the needed boundary conditions at $r = 0$ and $r = \infty$ respectively, the physical solution in the matching region must be a linear combination of either of these solutions. The physical linear combinations ($\overrightarrow{\psi}^{\text{core}}$ and $\overrightarrow{\psi}^{\text{LR}}$) are written in terms of the S -matrix states, Eqs. (2.17) and (2.18), and yet undetermined expansion coefficients B_i^{core} and B_i^{LR} :

$$\overrightarrow{\psi}^{\text{core}}(r) = \underline{M}^{\text{core}}(r) \overrightarrow{B}^{\text{core}} = \frac{1}{i\sqrt{2}} [\underline{f}^+(r) \underline{S}^{\text{core}} - \underline{f}^-(r)] \overrightarrow{B}^{\text{core}} \quad (2.21)$$

$$\overrightarrow{\psi}^{\text{LR}}(r) = \underline{M}^{\text{LR}}(r) \overrightarrow{B}^{\text{LR}} = \frac{1}{i\sqrt{2}} [\underline{f}^-(r) \underline{S}^{\text{LR}} - \underline{f}^+(r)] \overrightarrow{B}^{\text{LR}}. \quad (2.22)$$

These two physical solutions must be identical. Thus, equating Eq. (2.21) to Eq. (2.22) somewhere in the matching region ($\overrightarrow{\psi}^{\text{core}}(r_0) = \overrightarrow{\psi}^{\text{LR}}(r_0)$) yields an equation for the coefficients $\overrightarrow{B}^{\text{LR}}$,

$$[\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)] \overrightarrow{B}^{\text{LR}} = 0, \quad (2.23)$$

along with a two equations relating $\overrightarrow{B}^{\text{core}}$ and $\overrightarrow{B}^{\text{LR}}$:

$$\overrightarrow{B}^{\text{LR}} = -\underline{S}^{\text{core}} \overrightarrow{B}^{\text{core}} \quad (2.24)$$

$$\overrightarrow{B}^{\text{core}} = -\underline{S}^{\text{LR}}(E) \overrightarrow{B}^{\text{LR}}. \quad (2.25)$$

A nontrivial solution of these equations (2.23 and either 2.24 or 2.25) exists at a given energy E only if the following condition is satisfied:

$$\det [\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)] = 0. \quad (2.26)$$

The zeros of this equation give the bound energy levels E_n of the atomic electron bound to a multichannel positive ion in the presence of external fields. In these formulas I have explicitly written out the energy dependence of the long-range S -matrix $\underline{S}^{\text{LR}}(E)$ to emphasize that it varies rapidly as the energy is changed. The energy dependences of the other quantities, such as $\underline{S}^{\text{core}}$, are much weaker and can often be neglected. Additionally, it should be kept in mind that $\underline{S}^{\text{LR}}(E)$ is a strong function of the external field strengths B and F , whereas $\underline{S}^{\text{core}}$ does not depend on these parameters for the comparatively weak fields ($B < 100$ Tesla) under consideration here. As long as exact quantum mechanical S -matrices are used,

the quantization condition (2.26) is exact. More importantly, when a semiclassical approximation for $\underline{S}^{\text{LR}}$ is used, Eq. (2.26) becomes a semiclassical quantization condition for nonintegrable, multichannel atoms.

A number of researchers [77, 97, 98, 99, 100] have given quantization conditions similar to Eq. (2.26). This body of research shows that the quantization formula (2.26) represents a completely general method for quantizing multidimensional, nonintegrable systems. The only assumption I have made in its derivation is that at some radius (in the matching region), the effects of both the ionic core and the external fields on the electron can be neglected. Works by Prosen [99] and also Rouvinez and Smilansky [100] show that this assumption is not strictly necessary and I outline their approach here. To quantize a nonintegrable Hamiltonian of d spatial dimensions, configuration space is divided into two volumes V_a and V_b , which are separated by a $d - 1$ dimensional surface. This surface, called the surface of section, is equivalent to a configuration space version of the classical surface of section introduced by Poincaré to reduce the dynamics of an autonomous Hamiltonian system ($2d$ -dimensional phase space) to that of a discrete map of the surface onto itself. This surface of section is then used to define S -matrix states similar to Eqs. (2.17) and (2.18), along with S -matrices \underline{S}^a and \underline{S}^b for the two volumes. Their [99, 100] quantization condition,

$$\det [\underline{1} - \underline{S}^a(E)\underline{S}^b(E)] = 0, \quad (2.27)$$

is identical to the one I have derived here and shows the general nature of this approach.

However, the first formulation to use a Poincaré surface of section to quantize a nonintegrable Hamiltonian is Bogomolny's T -matrix method [97]. In this breakthrough work, Bogomolny derived a semiclassical quantization condition,

$$\det [\underline{1} - \underline{T}(E)] = 0, \quad (2.28)$$

for nonintegrable systems in terms of the “transfer matrix” $\underline{T}(E)$, which iterates a quantized version of the Poincaré map. In his work, the matrix $\underline{T}(E)$ is defined only semiclassically and is shown to be finite and unitary in the limit $\hbar \rightarrow 0$. Rouvinez and Smilansky [100] have shown that $\underline{T}(E)$ is equal to the product $\underline{S}^a(E)\underline{S}^b(E)$ in the same limit.

These works elucidate some insightful properties of quantization conditions written as a secular determinant involving finite, unitary S -matrices. A few of these properties are presented here for the case studied in this thesis, namely, an atomic electron in external fields. As Bogomolny demonstrates, because the S -matrices are finite and unitary, the secular determinant, Eq. (2.26), can be identified as a dynamical (or Selberg) zeta function [101, 102] $\zeta_s(E)$:

$$\zeta_s(E) = \det [\mathbb{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)]. \quad (2.29)$$

It is called a zeta function because it shares many interesting properties with the well known Riemann zeta function [103] $\zeta(s)$ along the line $s = 1/2 + it$. An excellent discussion of these remarkable connections can be found in the text of Brack and Bhaduri [24]. Two such properties that $\zeta_s(E)$ shares with the Riemann zeta function are the existence of a functional equation,

$$\zeta_s(E) = e^{2\pi i \tilde{N}(E)} \zeta_s^*(E), \quad (2.30)$$

and the so called Riemann-Siegel relation,

$$\zeta_s(E) = G(E) + e^{2\pi i \tilde{N}(E)} G^*(E). \quad (2.31)$$

The quantity $\tilde{N}(E)$ is the mean number of states with energy less than E , which is simply

$$\tilde{N}(E) = \int \frac{d^d p d^d x}{(2\pi\hbar)^d} \Theta(E - H(\vec{p}, \vec{x})) \quad (2.32)$$

for d degrees of freedom. In general, the $G(E)$ in Eq. (2.31) can be written as a finite sum over traces of powers of the matrix $\underline{S}^{\text{core}} \underline{S}^{\text{LR}}$, $\underline{S}^{\text{a}} \underline{S}^{\text{b}}$ or \underline{T} . By no means is this discussion of the dynamical zeta function complete; rather my goal has been to sketch the relationship between my work and that of others. The one new aspect of my work that has not been noted in the literature thus far is that functions such as $\det [\mathbb{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)]$ have the properties, Eqs. (2.30) and (2.31), of a dynamical zeta function even when exact quantum mechanical S -matrices are used. Previously, the dynamical zeta function has only been used in the context of semiclassical approximations. Thus, I propose that when exact S -matrices are used, Eq. (2.29) represents a quantum-mechanical zeta function.

One final relationship [100] expresses the density of states,

$$g(E) = \sum_n \delta(E - E_n), \quad (2.33)$$

in terms of the zeta function, Eq. (2.29), and the mean density of states $\tilde{g}(E) = \frac{d\tilde{N}(E)}{dE}$:

$$g(E) = \tilde{g}(E) - \frac{1}{\pi} \text{Im} \frac{d}{dE} \ln \det [\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)]. \quad (2.34)$$

This relationship shows that the matrix $[\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}(E)]$ controls the oscillating part of the density of states. Now I show that this matrix also controls the normalization of the bound states.

2.2.3 Normalization

At a bound state energy E , the physical wavefunction $\vec{\psi}_E(r)$ takes the form of the S -matrix states, Eq. (2.21) or (2.22), in the matching region. A study of the normalization of these states gives further insight into the physics of the bound states of the Rydberg electron. The normalization condition derived here is similar to that of Aymar *et al.* [68], and uses the method given in Greene [90]. As with the quantization condition (2.26), an important feature of the normalization condition is that it depends only on the matrix $[\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}]$. The beginning point of the derivation is the familiar normalization condition, written in terms of the multichannel radial wavefunction $\vec{\psi}_E(r)$ (either Eq. 2.21 or 2.22):

$$\int_0^\infty dr \left| \vec{\psi}_E(r) \right|^2 = 1. \quad (2.35)$$

Integrals (or sums) over the angular and spin degrees of freedom are not present because the channel functions are assumed to be orthonormal. At first glance it appears that this integral requires the physical wavefunction at all radii. A well known trick of QDT uses Green's theorem to convert the volume integral to a surface integral in the matching region [90]. This is advantageous because the S -matrix forms, Eqs. (2.21) or (2.22), of $\vec{\psi}_E(r)$ can then be used. The transformation to a surface integral,

$$\begin{aligned} \int_a^b dr \vec{\psi}_E^\dagger(r) \vec{\psi}_E(r) &= \lim_{E' \rightarrow E} \int_a^b dr \vec{\psi}_{E'}^\dagger(r) \vec{\psi}_E(r) \\ &= \lim_{E' \rightarrow E} \frac{1}{2(E' - E)} \mathbf{W} \left[\vec{\psi}_{E'}^*, \vec{\psi}_E \right]_a^b, \end{aligned} \quad (2.36)$$

involves the Wronskian,

$$\mathbf{W} \left[\vec{\psi}_{E'}^*, \vec{\psi}_E \right] = \vec{\psi}_{E'}^\dagger \frac{d\vec{\psi}_E}{dr} - \frac{d\vec{\psi}_{E'}^\dagger}{dr} \vec{\psi}_E, \quad (2.37)$$

evaluated at the end points $[a, b]$ of the integration range. This formula is derived by first writing down the Schrödinger equations for $\vec{\psi}_E$ and $\vec{\psi}_{E'}^\dagger$:

$$\frac{1}{2} \vec{\psi}_E'' + (E - \underline{V}) \vec{\psi}_E = 0 \quad (2.38)$$

$$\frac{1}{2} \vec{\psi}_{E'}^{\dagger''} + \vec{\psi}_{E'}^\dagger (E' - \underline{V}) = 0. \quad (2.39)$$

Left multiplying Eq. (2.38) by $\vec{\psi}_{E'}^\dagger$ and right multiplying Eq. (2.39) by $\vec{\psi}_E$, subtracting the two and using Green's theorem on the result gives Eq. (2.36). To use Eq. (2.36) to normalize the wave function (2.35) the range of integration is broken up into two integrals,

$$\int_0^\infty dr \left| \vec{\psi}_E(r) \right|^2 = \int_0^{r_0} dr \left| \vec{\psi}_E^{\text{core}}(r) \right|^2 + \int_{r_0}^\infty dr \left| \vec{\psi}_E^{\text{LR}}(r) \right|^2, \quad (2.40)$$

where the intermediate radius r_0 is chosen to be somewhere in the matching region. When Eq. (2.36) is used for each term on the right side of Eq. (2.40), the normalization condition for a bound state at energy E_n becomes:

$$1 = \lim_{E' \rightarrow E} \frac{1}{2(E' - E_n)} \left(\mathbf{W} \left[\vec{\psi}_{E'}^{\text{core}*}(r_0), \vec{\psi}_{E_n}^{\text{core}}(r_0) \right] - \mathbf{W} \left[\vec{\psi}_{E'}^{\text{LR}*}(r_0), \vec{\psi}_{E_n}^{\text{LR}}(r_0) \right] \right). \quad (2.41)$$

To obtain this result one must use the fact the wavefunctions $\vec{\psi}_{E_n}^{\text{core}}$ and $\vec{\psi}_{E_n}^{\text{LR}}$ vanish at $r = 0$ and $r = \infty$ respectively. Because r_0 is in the matching region, the S -matrix forms of $\vec{\psi}^{\text{core}}$ (2.21) and $\vec{\psi}^{\text{LR}}$ (2.22) can be used in Eq. (2.41) along with Eq. (2.24), $\vec{B}^{\text{LR}} = -\underline{S}^{\text{core}} \vec{B}^{\text{core}}$, to give:

$$1 = \lim_{E' \rightarrow E_n} \frac{1}{2(E' - E_n)} \vec{B}^{\text{core}\dagger} \left(\underline{\mathbf{W}}_1 - \underline{S}^{\text{core}\dagger} \underline{\mathbf{W}}_2 \underline{S}^{\text{core}} \right) \vec{B}^{\text{core}}, \quad (2.42)$$

$$\underline{\mathbf{W}}_1 = -\frac{1}{2} \mathbf{W} \left[\underline{f}_{E'}^-, \underline{S}^{\text{core}*} - \underline{f}_{E'}^+, \underline{f}_{E_n}^+ \underline{S}^{\text{core}} - \underline{f}_{E_n}^- \right], \quad (2.43)$$

$$\underline{\mathbf{W}}_2 = -\frac{1}{2} \mathbf{W} \left[\underline{f}_{E'}^+ \underline{S}^{\text{LR}*}(E') - \underline{f}_{E'}^-, \underline{f}_{E_n}^- \underline{S}^{\text{LR}}(E_n) - \underline{f}_{E_n}^+ \right]. \quad (2.44)$$

The matrices $\underline{\mathbf{W}}_1$ and $\underline{\mathbf{W}}_2$ can then be simplified using the definition of the Wronskian (2.37) and the Wronskians of \underline{f}^\pm given in Eqs. (2.2) and (2.3). Finally, the limit $E' \rightarrow E_n$ is taken using l'Hospital's

rule. After some algebra, and using Eq. (2.23), the final form of the normalization condition reads:

$$1 = \frac{1}{2\pi} \vec{B}^{\text{LR}\dagger} \frac{d}{dE} i (\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}}) \vec{B}^{\text{LR}}. \quad (2.45)$$

As in the quantization condition, the matrix $(\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}})$ controls the normalization of the bound states. As Harmin's work [83] on the Stark effect demonstrates, normalization constants such as this matrix are closely related to the density of states of the physical system. This is consistent with Eq. (2.34) that relates the quantum density of states to this matrix. In addition, in the next chapter the matrix $(\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}})^{-1}$ appears as a “density of states matrix” in the atomic photoabsorption cross section.

Alternatively, as Aymar *et al.* [68] point out, the normalization condition (2.45) can be expressed in terms of the Hermitian time delay matrices [104] for the core and long-range regions:

$$\underline{Q}^{\text{core(LR)}} = i \underline{S}^{\text{core(LR)}} \frac{d \underline{S}^{\text{core(LR)}\dagger}}{dE}. \quad (2.46)$$

The result,

$$1 = \frac{1}{2\pi} \vec{B}^{\text{LR}\dagger} \left(\underline{Q}^{\text{core}\dagger} - \underline{Q}^{\text{LR}} \right) \vec{B}^{\text{LR}},$$

shows that the normalization of the bound states involves a sort of balance between the physical time scales (encapsulated in $\underline{Q}^{\text{LR}}$ and $\underline{Q}^{\text{core}}$) in the core and long-range regions.

2.3 Discussion

In the previous section, ideas from scattering theory and QDT were used to study Rydberg states of atoms in static external electromagnetic fields. The following picture of the electron's motion undergirds this approach: the state of the Rydberg electron is pictured as a time-independent scattering process where the electron scatters repeatedly off the core and long-range regions each time returning to a radius in the “matching region” where it sees a pure Coulomb potential. The S -matrix states, Eqs. (2.17) and (2.18), formalize this idea by introducing two unitary S -matrices $\underline{S}^{\text{core}}$ and $\underline{S}^{\text{LR}}$. Using these S -matrix states I have derived a quantization condition (2.20) and a normalization condition (2.45) for the bound states of the Rydberg electron. These two equations, which are the main results of this chapter, begin to show that the most important physics of the electron is contained in the matrix $(\underline{1} - \underline{S}^{\text{core}} \underline{S}^{\text{LR}})$.

This approach of dividing configuration space into two regions and defining an S -matrix for each region is advantageous for a number of reasons. First, S -matrices are ideally suited to semiclassical approximations. In Ch. 5 I derive such an approximation for the long-range S -matrix using a semiclassical Green's function. Semiclassically, $\underline{S}^{\text{LR}}$ is written as a sum over classical orbits, closed-orbits, that are launched outward from a sphere in the matching region, scatter off the long-range fields and then return to the sphere after time T . I show that the classical action S_k (not to be confused with the matrix $\underline{S}^{\text{LR}}$) of each such orbit contributes to the phase of the S -matrix in the form (see Eq. (5.39)):

$$\underline{S}^{\text{LR}}(E) = \sum_k \underline{A}_k e^{iS_k(E)}. \quad (2.47)$$

The matrix \underline{A}_i of each orbit depends on the stability, Maslov index, and initial and final angles of the orbit. While the results of this chapter can be written in terms of either K -matrices or R -matrices, the semiclassical approximations for these matrices are needlessly cumbersome compared to that of the S -matrix (2.47).

Second, S -matrices give important physical insight not available in other approaches. This can be seen by looking at the trace of the time delay matrix for the long-range region in a semiclassical approximation. A substitution of the semiclassical form of $\underline{S}^{\text{LR}}$, Eq. (2.47), into the definition of the time delay matrix, Eq. (2.46), gives,

$$\text{Tr}(\underline{Q}^{\text{LR}}(E)) = \text{Tr}\left(i\underline{S}^{\text{LR}} \frac{d\underline{S}^{\text{LR}\dagger}}{dE}\right) = \sum_k T_k(E) \alpha_k, \quad (2.48)$$

where $T_k(E) = \frac{dS_k}{dE}$ denotes the period of the k th classical orbit and $\alpha_k = \text{Tr}(\underline{A}_k \underline{A}_k^\dagger)$ is a number indicating the relative importance of the orbit. This shows that the S -matrix $\underline{S}^{\text{LR}}$ gives direct access to the time domain physics of the Rydberg electron. Chs. 4 and 5 show that the quantitative details of this time domain physics in $\underline{S}^{\text{LR}}$ can be extracted by Fourier transforming $\underline{S}^{\text{LR}}(E)$ into the time domain.

Third, and finally, dividing configuration space into two regions leads to an efficient approach. Once the long-range S -matrix has been calculated for a given configuration of external fields, the observables of many different atoms in that configuration of fields can be calculated by simply using the $\underline{S}^{\text{core}}$ appropriate to each atom.

Of course, the best argument for formulating the theory in terms of S -matrices is their usefulness. This chapter has begun to build a case for this viewpoint by showing that the S -matrices $\underline{S}^{\text{LR}}$ and $\underline{S}^{\text{core}}$ determine the bound state physics of an atomic electron in the presence of an external electric or magnetic field. In the next chapter, I continue along these lines, exploring the relationship between the S -matrices and the atomic photoabsorption cross section.