

Chapter 6

Conclusion

On a practical level, this dissertation has considered the physical properties of two highly excited diatomic systems, one commonplace, and naturally occurring throughout the universe, and one exotic, and likely to be observed under only carefully controlled laboratory conditions. On a conceptual level, however, these studies share a common philosophical framework with respect to the way in which they approach the process of scattering for Rydberg electrons in quantum mechanical systems.

From the standpoint of classical mechanics, scattering is understood as a discrete event or series of events associated with the changing trajectories of a set of particle or bodies or bodies. A pair of scattering billiards, for example, will move along a flat surface in straight line until they hit one another, experience an instantaneous redistribution of their total energy and momentum (perhaps with some dissipation due to inelasticity), and then continue away along altered trajectories. A satellite undergoing a close encounter with a planet will slingshot rapidly through its gravitational field in a hyperbolic orbit, emerging along a new asymptotic trajectory with a modified direction and velocity. Scattering, by nature, is a *localized* process. It takes a strong interaction that occurs during a short period of time and is confined to a limited region of space, and reduces it to an overall effect in terms of the alteration of a system's trajectories in free space.

In quantum mechanics, the picture of particles traveling along trajectories and

undergoing isolated events must typically be abandoned. The solution to tunneling through a barrier, the first quantum scattering calculation that any young physicist is likely to encounter, is solved entirely in terms of wavefunctions and matching conditions; the solution in each region is solved separately, and the solutions are joined together by the conditions of continuity and smoothness across the boundaries. This picture is entirely *delocalized*. The solutions are continuum solutions that extend from negative infinity to positive infinity, and there is no “event” associated with the calculation. A sufficiently large number of solutions may be superposed, of course, to give a localized wavepacket, and propagating that wavepacket according to the time-dependent Schrödinger equation will recover a dynamical behavior recognizably similar to the classical case. But the preparation of such a packet will necessarily involve states with a range of energies, whereas many interesting quantum mechanical measurements are associated with experiments for which the preparation of such wavepackets is difficult or impossible. A common situation is that of experimental continuous-wave spectroscopy, where a monoenergetic photon source (like a laser) excites an atomic or molecular system with a single, well-defined energy.

The challenge of highly excited quantum mechanical systems, such as Rydberg atoms and molecules, is that they occupy an intermediate status between the quantum and classical understandings of scattering. On one hand, they are clearly scattered by localized interactions. The total volume through which a Rydberg electron moves is typically quite large compared to the volume in which it has a complicated interaction with a scattering body. One is logically motivated to find some way of exploiting the spatial confinement of this interaction in order to simplify the task of solving the Schrödinger equation. On the other hand, the interactions themselves are clearly quantum mechanical in nature, such that it would be disastrous to attempt to treat an electron scattering from a molecule as if it were something like a marble scattering from a set of bowling balls connected by springs. The exchange of energy and momentum between a scattering

electron and a molecule is a function of inherently quantum mechanical properties such as phase, wavelength, spin, quantized orbital angular momentum, and quantized molecular excitation modes. The solution must therefore be quantum mechanical in form. The possibility of successfully combining advantageous features of both perspectives is realized by quantum defect theory, which interprets complex short-range interactions in terms of their net effect on long-range parameters like the quantum defects or phase shifts.

In Chapter 2, quantum defect theory was introduced as a paradigm for thinking about the effect of core scattering on a Rydberg state. The electron moves mostly in a region far separated from the core, under the influence of a long-range Coulomb potential, and therefore has a solution that resembles the hydrogenic wavefunctions; the only effect of the core is to shift the energy of these wavefunctions in a way that is dependent on the orbital angular momentum, but at least to a good approximation is independent of the electron's long-range behavior. In the wavefunction itself, this manifests as a phase parameter that mixes the regular and irregular Coulomb functions. In effect, the quantum defect formalism divides the problem into a short-range solution region and a long-range solution region, and describes the effect of the short-range physics on the long-range solution in terms of the minimum number of necessary parameters. For a problem with multiple scattering channels, the scattering matrix suffices to specify the probability amplitude for inelastic scattering from one type of channel to another. Although this is fully quantum mechanical, the classical picture of scattering as a localized event that modifies particle trajectories has been restored. In semiclassical terms, the electron occupies a closed orbital that, once per orbital period, scatters from the core in such a way as to accumulate an additional phase shift, and transfer incoming probability flux in one channel to outgoing flux in the others. The efficacy of this approach was demonstrated for the diatomic system HD, but the method generalizes naturally to any Rydberg system, atomic, diatomic, or polyatomic. With respect to the problem of

describing overlapping Rydberg series of resonances in the electronic continuum, there is presently no other method that rivals the capabilities of quantum defect methodology to efficiently reproduce resonant features in the scattering cross-section.

In Chapter 3, a single long-lived Rydberg stationary state is created, and the effect of perturbation by the presence of a second particle that physically impinges on the Rydberg wavefunction is considered. This situation is similar to that of Rydberg excitation in the previous chapter, in the respect that electron-core interaction may still be described most efficiently by quantum defects, but the second scattering center creates an additional set of boundary conditions that must be satisfied. Just as the modification of a Coulomb potential could be expressed in terms of phase-like quantum defect parameters, so also the short-range scattering of the electron by a neutral perturber can be fully described in terms of an overall phase shift in each channel. These phase shifts provide the basis for a zero-range pseudopotential approximation that performs with accuracy comparable to the more conventional approach of diagonalizing the Hamiltonian in an L^2 basis. In classical terms, one might think about the difference between a detailed modeling of the local interaction between two colliding billiard balls, with infinitesimal deformations during the moment of contact accounting for the exchange of impulse, and an hard sphere approximation that treats the collision as truly instantaneous. The first level of detailed analysis might be necessary to account for slight inelasticity of the collision, or the transfer of translational motion into rotation for off-center collisions, but once the functional dependence of these effects was known, they could be incorporated directly into the hard-sphere model as various corrections and coefficients without the need to repeated the detailed calculation. The parameterization of Rydberg-neutral scattering in terms of phase shifts that depend only on the energy and angular momentum of the electron accomplishes a similar reduction of the detailed short-range behavior in terms of its collective asymptotic effect.

Chapter 4 implements the separation between the scattering region and the exter-

nal free-electron region in an even more literal sense, by using the Coulomb Green's function to write an exact integral equation solution in the outer region, and match it onto the phase-shift adjusted short-range solution close to the perturber. Since the Green's function serves as a propagator in the energy representation, this may be viewed quite literally as repeatedly colliding the electron with the perturber, and using the boundary matching condition to select out the stable closed orbit trajectories of the motion. In fact, modern semiclassical theory allows this picture to be implemented directly, with a coherent summation over the two closed Coulomb orbits that pass through a given point and begin and end on a small sphere bounding the perturber. The constructive interference between the paths is responsible for the distinctive nodal pattern of the wavefunction that accounts for its resemblance to the ridged shell of a trilobite.

The Rydberg state localized-scattering picture is certainly powerful with respect to the task of describing highly excited and continuum electronic states. This raises the question of whether one can retain the advantages of this philosophy, while at the same time including the nuclear continuum states that arise in the context of dissociation. Chapter 5 provides a demonstration of several approaches to extending multichannel quantum defect theory or R-matrix theory to systems with such a double continuum, including one that is entirely original, the method of Siegert channel states.

This dissertation has refined and extended a set of existing tools from the fields of resonance theory, quantum defect theory, and multichannel spectroscopic analysis in order to describe two rather dissimilar diatomic systems that arise from Rydberg electron excitation. From this foundation, there are many directions that could be pursued with respect to verifying, improving, or applying these ideas. In some cases, this may simply mean coming to a better understanding of the limitations of these methods. The machinery of quantum defect theory, for example, as powerful as it often proves to be, leaves no obvious procedure for improvement of accuracy. Unlike perturbation theory, there are no "higher level terms" available in the theory to systematically improve the

convergence of a solution, and unlike variational methods, there is no guarantee of a lower or upper bounding of the calculated values. The incorporation of effects arising from energy dependence of the quantum defect parameters, for example, or symmetry breaking effects like the loss of *gerade-ungerade* symmetry in HD and Jahn-Teller couplings in triatomics, must usually be added to the model on a somewhat *ad hoc* basis. This increases the importance of confirming the results of such calculations, either by more rigorous computational methods, or by direct experimental observation.

For the long-range Rydberg bound states, the first crucial test of the theory would involve experimentally confirming their existence by means of some spectroscopic signature. At present, the most difficult aspect of preparing these states lies in the creation of a high-enough density cold dilute gas sample. Most modern magneto-optical traps are capable of generating densities in the range of 10^{10} - 10^{11} atoms per cm^{-3} ; the population of nearest-neighbor pairs with the correct separation to form resonance-induced bound states (e.g., at 500-1000 Bohr radii for $n=30$ -70) would be greatly enhanced at densities only a few orders of magnitude larger than this. As a possible alternative, the existence and structure of molecular potential curves might be deduced from the observation of satellite lines even at temperatures above those favorable for the formation of bound states. On the theoretical end, further refinement of the theory in this paper (particularly with regard to the handling of fine and hyperfine structure) would be advantageous.

If the existence of such states is confirmed, other opportunities for application-oriented theoretical study could be investigated more thoroughly. The large permanent dipole moments attached to these states makes the prospect for alignment-based applications particularly appealing. For example, if a sample of Rydberg molecules were prepared and oriented along a common axis, and a beam of slow electrons passed through the sample in the direction of that axis, one might imagine the electrons displaying a diffraction pattern suggestive of the intricate nodal structure of the electronic wavefunc-

tion. Another possibility, prompted by the observation that (to a good approximation) the effect of the perturber is simply to mix atomic states, might be the creation of a similarly shaped electronic wavefunction in the absence of any perturber at all, perhaps by the use of pulsed multipole electric fields [167]. A third idea might involve the study of Rydberg-state induced dissociation of diatomic or polyatomic perturbers *via* dissociative attachment, as initially proposed in the work of Dubov and Rabitz [65, 66] in the context of considering laser-assisted exchange reactions.

As noted in the conclusion to Chapter 5, the utility of the Siegert state method has already been demonstrated beyond the case of molecular hydrogen. The most direct route to generalize the method to polyatomic molecules is probably that used in [28], based on a transformation of the nuclear motion to hyperspherical coordinates. One might also envision finding a technique for calculating multidimensional Siegert pseudostates, with the possibility of outgoing flux on several different surfaces or hypersurfaces in a multidimensional volume. In the two-dimensional case, for example, it could provide a new approach to the handling of two-electron systems with an accessible double ionization continuum, perhaps in conjunction with R-matrix methodology. Even more complicated molecules might be analyzed by isolating a subset of particularly “active” normal modes, and defining the Siegert spectrum in the normal mode coordinates directly.

The study of resonant effects in near-threshold electron-molecule scattering processes may provide the first step toward a greater understanding of resonant effects in larger molecules with similar local structure. The work of Burrow and coworkers, for example, has described resonant scattering properties of electrons from both chloroalkanes and DNA bases using a model that assumes a single electronically active bond, with subsequent vibrational coupling to the other bonds of the molecule [168, 169]. And the work of Gianturco and Lucchese has suggested that one of the most important contributions to DNA radiation-induced decay channels involves the creation of photoionized elec-

trons that undergo low-energy dissociative attachment, a process that depends vitally on energy redistribution between electronic and nuclear excitation modes [170, 171].