

## Chapter 1

### Introduction

The progress of scientific thought has, at several critical junctures in history, depended essentially on something that can only be regarded, with the advantage of hindsight, as an exceptional stroke of good luck. The theory of celestial mechanics, as first developed by Johannes Kepler, involved several levels of fortunate happenstance: Kepler was lucky to have selected Mars for his studies, with its notably elliptical orbit capable of detection even by the rudimentary measurements of his era; he was lucky that the law he was in the process of discovering involved orbits that traced conic sections, a class of geometric constructs that had been the object of extensive study by the ancient Greeks for purely aesthetic reasons; and he was lucky that the motion of planets in the solar system, due to the mass disparity between them and the sun, could be described so well at the level of approximation as a set of noninteracting two-body systems. Without the benefit of Kepler's good fortune, Copernicus would not have been so quickly vindicated, nor would the foundation for Newton's subsequent development of gravitation been so firmly established.

By coincidence, it would be another researcher named Johannes who, three centuries later, traced Kepler's steps in recognizing an empirical law derived from the same inverse-square force law as Kepler's orbital mechanics— although, like Kepler, Johannes Rydberg had little appreciation of the physical basis for his empirical formula. (Ironically, his doctoral dissertation, written in mathematics before his interests turned to

physics, had been on the subject of conic sections.) As with Kepler's fortuitous choice of Mars, Rydberg had the benefit of several spectral lines of hydrogen (what we now know as the Balmer series) that lay well within the visible region of the spectrum. These lines had in 1885 been identified by yet another Johann, the Swiss schoolteacher Johann Jacob Balmer, as being well-characterized by the formula  $\lambda \propto n^2/(n^2 - 2^2)$  [1], although Rydberg was not aware of this at the time he began his study. Rydberg, working from a larger library of spectroscopic data for hydrogen and the alkali metals, was able to successfully generalize Balmer's form of the transition frequency in 1888, with the now-familiar result [2]

$$\frac{n}{N_0} = \frac{1}{(m_1 + c_1)^2} - \frac{1}{(m_2 + c_2)^2}. \quad (1.1)$$

The names of the variables are here intentionally presented using Rydberg's original choice of symbols:  $n$  is the wavenumber of the emitted light,  $N_0$  is the eponymous constant named in Rydberg's honor, and  $m_1$  and  $m_2$  are positive integers. The appearance of the additional constants  $c_i$  was, happily enough, the **only** modification necessary to extend the hydrogenic formula to the analysis of alkali spectra. And this, of all the providential manifestations of natural simplicity considered thus far, is the one with which this thesis shall be most properly concerned.

It would be an excusable generalization for one to observe that, in practical terms, Rydberg states are the only multiparticle states that are quantitatively understood at anything approaching the celebrated level of success achieved by quantum mechanics for ground state energies and wavefunctions. The tools of quantum chemistry that have so far been developed for the treatment of many particle systems rely chiefly on variational approaches that minimize variables (most commonly the total energy) subject to constraints, and as such generalize poorly to excited states. Only in the last twenty years have techniques for excited state ab initio calculation begun to achieve

reasonable success, and even then only at great computational expense [3]. The Rydberg states arising from a Coulombic potential, uniquely and fortuitously, pass over into a limit which reduces the complex electronic correlations into a simply parameterized form that reflects a nearly-exact integrability of the Schrödinger equation for the electronic potential. As a consequence, even molecular Rydberg spectra with a dizzying array of closely spaced resonances are still naturally tractable with respect to spectroscopic assignment. The more highly excited a Rydberg state becomes, the more it acquires the character of a perturbed hydrogenic state, and thus the more regular and predictable the associated structure is expected to become.

With sufficiently accurate spectroscopic methods, deviations from the general expression given above begin to emerge, reflecting a variety of subtle perturbative effects on the spectrum that would be difficult to detect through other methods. The analysis of Rydberg spectra effectively extracts quantitative information about the spatial distribution of electrons and nuclei in the core, as well as the partitioning of energy between possible modes of core state excitation. One important class of perturbative effects is associated with core anisotropy, arising from either the electrostatic multipole moments of the core geometry or induced polarization of the core electrons. Other small spectroscopic shifts may be attributed to relativistic modification of the motion and interaction of the Rydberg electron, including the so-called Casimir force. These corrections are all manifestations of the alteration of the long-range Coulombic potential, and can be expressed rather intuitively, albeit often non-trivially, as additional terms in the electronic Hamiltonian defining Rydberg motion. While these terms may possess complex tensorial character, they are essentially adiabatic in nature, and thus remain amenable to treatment within the familiar framework of adiabatic approximations.

Another important class of spectroscopic signatures for Rydberg-core interaction involves the sensitivity of the Rydberg electron to short-range many-particle dynamics in the immediate vicinity of the core structure. Due to the disproportionality of the

spatial probability distribution of the highly excited electron relative to that of the (at most weakly excited) core, the volume over which such interactions can contribute is necessarily small. For Rydberg states with more than a few quanta of angular momentum, the resultant centrifugal barrier shields the core entirely, and all short-range effects are buried deep inside of the inner turning point of the effective potential. For any case where the Rydberg wave function extends even slightly into the core volume, however, the core may exert substantial effects on the solution within that volume, and thereby alter the stationary superposition of hydrogenic solution states in the asymptotic Coulomb region as well. Further discussion of the origin of these effects will be deferred until Chapter 2; for the moment, it suffices to note that they require a fundamentally non-Born-Oppenheimer description. When the electron is far from the core, it has relatively little kinetic energy, and its motion cannot be considered “fast” on the time scale of core dynamics; when the electron is close to the nucleus, it has enormous kinetic energy due to proximity to the singularity of the Coulomb potential, and enters and exits the core volume on a time scale much faster than any adiabatic rearrangement of energy within the core. In summary, one may instructively observe that the Rydberg electron lives in one region of space where the Born-Oppenheimer potential is valid but the single particle approximation fails due to strong correlation with the other electrons and coupling with the core degrees of freedom, and one region of space where the single particle approximation is valid but the Born-Oppenheimer approximation fails due to the decoupling of the slow Rydberg electron from the geometry and orientation of the core state.

## 1.1 Historical development of experimental technique

The separation between lines arising from the manifolds of a hydrogenic energy spectrum diminishes rapidly with increasingly primary quantum number  $n$ , as  $\frac{1}{n^3}$ . The difference between the  $n = 99$  and  $n = 100$  manifolds is already less than half a

wavenumber. Selective excitation of a particular state either within or near a particular manifold (when, for example, the usual selection rules are broken by the introduction of a small external static electric field) demands even greater control over the energy and linewidth of the incident light. The extraction of detailed structure within the Rydberg spectrum has thus been dependent upon advances in the efficiency with which light can be produced at both high intensity and narrow bandwidth. Prior to the advent of modern laser optics, this required the use of dispersive instruments such as prisms and diffraction gratings to isolate monochromatic components of a broadband source. The task was further complicated by the necessity of working under vacuum conditions due to the strong continuum absorption of common background gas components in the ultraviolet, where Rydberg transitions of atoms and small molecules are most commonly observed. Molecular oxygen becomes opaque below 1850 Å, and molecular nitrogen below 990 Å. (For a survey of some early difficulties of the development of spectroscopy in the VUV, see [4].)

In light of these experimental difficulties, it is understandable that high-resolution Rydberg spectroscopy did not attain sufficient resolution to detect small (i.e., on the order of a wavenumber) structure and shifts until the late 1960s and early 1970s. The earliest high resolution discrete absorption spectrum of molecular hydrogen was that conducted by Herzberg [5], and the first high resolution continuum spectrum was that of Dehmer and Chupka [6]. These results, improving on previous resolution by as much as two orders of magnitude, not only successfully resolved the rotational and vibrational separations of the molecular spectrum with precision better than a fraction of a wavenumber, but also were capable of accurately defining line widths and shapes to an extent that prompted the development of new theory describing strong energy dependence (i.e., resonant effects) of the photoexcitation cross-sections with quantitative rigor.

The emergence of even better experimental methodology in the last twenty years

has continued to improve the quality of Rydberg spectroscopy. Noteworthy examples include the popularization of high-intensity synchrotron radiation sources, permitting even weak features in the spectrum to contribute an observable signal, and the introduction of narrow bandwidth laser sources extending into the far ultraviolet through the use of tunable lasers, frequency doubling, and higher harmonic generation. Laser technology has not only superseded the use of dispersive monochromators, but has also opened the door to exquisitely fine control over the phase and coherence properties of the incident light. Among the many delicate effects now accessible by experimental techniques are the tunneling between the vibrational potential wells of highly excited double-well adiabatic  $H_2$  potential curves [7], the breaking of  $g-u$  symmetry in HD, [8], singlet-triplet mixing near the  $H(n=1)+H(n=2)$  dissociation limit [9], and competition between dissociation and ionization decay dynamics in the regions of the  $H_2$  spectrum in an energy regime where multiple dissociative fragmentation channels are simultaneously open [10].

## 1.2 Emerging applications for Rydberg state theory

Much of the appeal of Rydberg states lies in their potential to serve as a bridge between classical and quantum mechanics. Traditionally, the former has been associated paradigmatically with macroscopic systems, and the latter with microscopic systems. In theory, of course, classical mechanics is merely the expression of certain limiting procedures necessary to extend quantum theory to systems with arbitrarily large particle numbers, energies, and state densities. With respect to the boundary between the classical and quantum regimes, one may identify two areas of burgeoning recent research interest: First, techniques to demonstrate explicitly quantum mechanical properties on a macroscopic (or at least mesoscopic) scale, and second, new methods to control or selectively influence the evolution of quantum systems.

Much of the renewed interest in atomic physics generally may be attributed to

rapid improvements in laser trapping and cooling technology. From the standpoint of Rydberg spectroscopy, the ability to cool atoms to temperatures to fractions of a Kelvin is especially appealing, since highly-excited states can survive for long times under such conditions, allowing their evolution over time to be systematically manipulated and externally directed toward a controlled outcome. Possibilities include arranging Rydberg atoms in an orderly spatial geometry, entangling them with one another, constructing Rydberg electron wavepackets that mimic classical particles or display long-time recurrence effects, and exploring the controlled or spontaneous transition of Rydberg atoms into molecules or plasmas.

The range and diversity of such work has been extensive enough that it can only be surveyed here by a selected subset of representative examples. Rydberg atoms have been proposed as a pathway to quantum information processing, either via a dipole blockade effect [11, 12], entanglement in superconducting cavities using microwave photons [13], or half-cycle pulses shaped using optimal control theory [14, 15]. A system of cold trapped atoms excited to high Rydberg levels has been observed to evolve spontaneously into a cold plasma, at temperatures four orders of magnitude lower than any other method of cold plasma generation, in a phase transition postulated to be analogous to the Mott transition in semiconductors [16, 17, 18, 19]. The angular momentum composition of Rydberg wavepackets has been selectively controlled by phase-locked laser pulses [20]. The coherent control of a four-wave mixing signal has been observed as a manifestation of the interference between Rydberg excitation pathways [21]. The collision potentials between Rydberg atoms have been examined in detail, revealing curve crossings at thousands of a.u. capable of supporting bound vibrational levels [22], which may already have been experimentally observed [23]. Finally, Rydberg states have been proposed as a sensitive probe of small electric fields and gas phase ion concentrations, as well as various other measurements of fundamental molecular constants like ionization potentials and ionic energy level structure [24].

Less attention has been paid to what might be termed “Rydberg chemistry”, the study of bond formation and dissociation processes facilitated or influenced by the presence of Rydberg electrons. Such applications would define a new field of conceptual overlap between the increasing interest in quantum control of chemical reaction products, in the physical chemistry community, and the atomic Rydberg investigations by the AMO community discussed above.

### 1.3 Outline of presented topics

In this thesis I explore a number of the properties of molecular Rydberg state solutions, and the calculation and analysis of spectroscopic observables. In the development of new techniques and predictions, one logically begins by working from the simplest cases toward the more complex, and the simplest of all molecules are homonuclear diatomics. I shall consider two varieties of diatomic Rydberg bound states, one being the more conventional case in which the molecular ion is bound by the core electrons, with the Rydberg electron serving as a probe of the core structure and dynamics, and the other being long-range molecules with two distantly separated centers in which the bonding is controlled by the Rydberg electron itself.

In Chapter 2, I introduce the basic concepts and vocabulary of scattering theory in an informal overview. The significance and origin of resonances is considered, with particular attention to their relationship to the different classes of motion that characterize the degrees of freedom that create resonant effects. I specialize to the example of molecular hydrogen, and move on to the consideration of multichannel spectroscopy, and how it can be described from the standpoint of a quantum defect formalism. The spectrum of the molecular hydrogen isotopomer HD is calculated by way of quantum defect theory in conjunction with application of Fano’s frame transformation procedure, followed by a critical assessment of the limitations of the approach.

Chapter 3 pursues the separate topic of the perturbed spectrum of a Rydberg

atom in the presence of a ground state atom or molecule. The interaction between the Rydberg electron and the perturbing atom or molecule is first considered at the level of a zero-range interaction approximation, where the particle is described by a delta function potential with a strength proportional to the energy-dependent generalization of the scattering length. This approximation yields an exact analytical result in degenerate perturbation theory for a hydrogenic Rydberg atom, if spin-orbit and other degeneracy-breaking terms can be neglected. The results of this approximation are tested by means of a more detailed finite-range model pseudopotential defined in a way that separates out scattered partial waves non-locally. Properties of the bound state potentials that arise from such interactions are noted and discussed.

Chapter 4 returns to the same problem, but instead treats it using a Green's function formalism. I demonstrate the ability of this method to reproduce the other methods of the previous chapter, both for the hydrogenic and finite quantum defect cases. The case of perturbation of a Rydberg molecule by a weak external electric field is considered, with example calculations. Finally, some relationships between semiclassical closed-orbit theory and the nodal pattern of the quantum wavefunction.

Chapter 5 revisits the diatomic photoionization spectrum, and introduces the complication of competing dissociative processes. The history of methods that treat competition with the dissociative continuum is reviewed, and the advantages and limitations of various methods are observed. As an alternative to these, I propose a new representation of coupling to the continuum, using a discretized pseudostate basis obeying Siegert boundary conditions. The properties of Siegert pseudostates are briefly summarized, and a recently developed method for their efficient generation is described. Using these pseudostates as a finite basis representation for the MQDT-frame transformation technique, it is shown that scattering into the ionization and dissociation continua can be treated simultaneously within a unified formalism.