# Photoionization, Photodissociation, and Long-Range Bond Formation in Molecular Rydberg States

by

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This thesis entitled:
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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

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Thesis directed by Prof. Chris H. Greene

The Rydberg spectra of atoms and small molecules offers an experimentally convenient probe for exploring the exchange of energy between Rydberg electrons and other forms of electronic, vibrational, and rotational excitation. This thesis investigates a series of special topics in the field of molecular Rydberg spectra, using a diverse set of theoretical techniques all designed to take advantage of the computational efficiency of the sorts of scattering parameterizations commonly associated with the field of quantum defect theory. In particular, I consider various mechanisms by which Rydberg electrons participate in the formation (bonding) and destruction (dissociation) of molecular states.

First, I review the methodology of multichannel quantum defect theory in molecular systems, demonstrating its versatility in reducing a complicated set of channel-coupled solutions into a physically observable photoionization spectrum with exceptionally high resolution, even in regions characterized by complex resonant structures with strong energy dependence. The utility of the Fano frame transformation is discussed, two approaches to the problem of extracting resonant effects via the delay of asymptotic boundary conditions are presented, and a case study featuring the molecular hydrogen isotopomer HD is examined in detail.

Second, I turn to the question of Rydberg electrons in the presence of both an ionic core and a neutral perturbing particle, extending certain basic features of the above philosophy to a two-center geometry. This system is predicted to give rise to a potential well that supports bound states, with a potential curve minimum existing at many hundreds or thousands of Bohr radii. The problem is first handled at the

level of a zero-range potential approximation, where the solution can be written by means of degenerate perturbation theory. This approach is compared to a more robust, but computationally expensive, description of the interaction in terms of a finite range model potential, requiring diagonalization of the Hamiltonian with respect to an $L^2$ basis. Some properties of these states are also noted. Next, a more powerful but difficult formulation using the Coulomb Green's function, subject to limiting boundary conditions at the position of the core and perturber, is derived. Finally, a semiclassical interpretation, corresponding to the trajectories of a point particle electron moving classically in a Coulombic field, is examined in detail.

Third, I return to the case of the diatomic Rydberg spectrum, this time extending the solution to accommodate dissociation pathways through the use of a Siegert pseudostate basis. Previously developed methods of treating the competition between ionization and dissociation are reviewed and evaluated. The Siegert basis is defined, together with an efficient procedure for its calcuation, and some of its unconventional properties are explicitly noted. The Siegert-MQDT method is applied to several reactive scattering or half-scattering processes, including photodissociation, dissociative ionization, and dissociative recombination.

## Dedication

To my grandfather, Edward H. Hamilton, who unlike myself was not merely acquainted with electrons, but could also teach them to perform useful tricks.

## Acknowledgements

A thesis is not so much the accomplishment of the mind of its author as it is the work of dozens of other minds being filtered through his own. The hope is that, in the course of the filtering, all that other work can directed toward a sharper focus, like water through a funnel or light through a lens.

My initial year at Colorado was challenging, and it seems appropriate to express my appreciation for those who helped me survive it. David Nesbitt, in addition to being a fine teacher (and based on his impromptu in-class barbershop performance, also a fine vocalist!), was a source of early encouragement. Carl Lineberger helped ease my transition by guaranteeing me a position my first summer out, when I was still figuring out where I wanted to go and what I wanted to do when I got there. My office mate Jeff Wright rescued me from certain of the more fiendish problems in Mr. Jackson's famous textbook on rather short notice, and displayed a reassuring combination of humor and good sense when the answers weren't so apparent to either of us.

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