

**Quantum and Semiclassical Scattering Matrix Theory for  
Atomic Photoabsorption in External Fields**

by

**Brian Ellison Granger**

B.S., Westmont College, 1994

A thesis submitted to the  
Faculty of the Graduate School of the  
University of Colorado in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
Department of Physics

2001

This thesis entitled:  
Quantum and Semiclassical Scattering Matrix Theory for Atomic Photoabsorption in External Fields  
written by Brian Ellison Granger  
has been approved for the Department of Physics

---

Chris H. Greene

---

John R. Cary

Date \_\_\_\_\_

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.

Granger, Brian Ellison (Ph.D., Physics)

Quantum and Semiclassical Scattering Matrix Theory for Atomic Photoabsorption in External Fields

Thesis directed by Professor Chris H. Greene

The photoabsorption spectra of Rydberg atoms in static, external electric and magnetic fields provide an excellent opportunity to study the properties of a nonintegrable physical system. This thesis develops a general theory for predicting and interpreting the photoabsorption spectra of these systems. Using ideas from both quantum-defect theory and semiclassical approximations, such as closed-orbit theory, I introduce scattering matrices to describe the final state of an electron in a photoabsorption experiment. The scattering matrices encapsulate all of the important physics of the system, and are related to important observables of the system, such as the bound state spectrum and the photoabsorption cross section.

Initially, the framework for calculating the photoabsorption cross section is presented in complete generality. An exact expression for the energy smoothed photoabsorption cross section is derived and is shown to provide a useful link between quantum-defect theory and semiclassical approximations. Although the formula is an exact result, it already contains many of the physical insights of semiclassical approximations about the time (or action) domain physics of the electron. Both the complications of multielectron atoms and arbitrary configurations of static, electromagnetic fields are included in the theory.

After the basic framework has been developed, semiclassical approximations are introduced for the specific case of an alkali-metal atom in an external magnetic field. I derive a semiclassical S-matrix to describe the scattering of the electron off the combined Coulomb and diamagnetic long-range potentials. The relationship of the semiclassical approximation to accurate quantum calculations is then explored.

Finally, the semiclassical S-matrix is used to construct a semiclassical formula for the photoabsorption cross section. Here, the focus is on the Fourier transformed cross section, or recurrence spectrum, which shows sharp peaks that correspond to certain quantum mechanical paths of the electron as it scatters off the long-range potentials. The semiclassical approximation of the cross section interprets

these quantum paths by correlating them with classical closed orbits of the electron. By taking a surprising cancellation between ghost and core-scattered orbits into account, a resumed semiclassical cross section is derived. This formula gives a convergent, semiclassical theory for the recurrence spectra of nonhydrogenic atoms. Results are presented for diamagnetic lithium and rubidium.

## **Dedication**

To my family with love.

## Acknowledgements

Like most things in life, this thesis could not have been completed without the encouragement and support of many people. I want to graciously thank everyone who has been a part of my experience of physics in graduate school.

Most importantly, my advisor, Chris Greene, has been a wonderful teacher and mentor to me. When I began in the group, Chris was bold enough to let me begin a project in an area of atomic theory that was new for both of us. I have appreciated his patience as I have struggled to learn the often tricky semiclassical methods used throughout this thesis. This patience has been a great gift to me and has allowed me to learn the methods well. At the same time, Chris has taught me to think about problems in physics using the ideas and tools of quantum-defect theory. From the beginning, Chris was convinced that semiclassical approximations were closely related to the scattering matrices of quantum-defect theory. This perspective has informed all of the work in this thesis. Most of all, I appreciate Chris's love of theoretical physics. This enthusiasm has rubbed off on me and has made my time in his group completely enjoyable.

I tend to learn physics best by talking with others. This has made the presence of the other members of Chris's group invaluable. Early on, Hugo van der Hart spent many hours teaching me about B-splines and R-matrix theory. In the past few years, I have appreciated many conversations with Edward Hamilton and Dörte Blume as well. In addition, from the day I arrived in Boulder, Fernando Perez has encouraged me towards theoretical physics and a strong life of the mind.

John Delos and his students and postdocs have also been a wonderful resource in this project. At first, the original articles of Du and Delos provided my primary training in semiclassical methods. Since

then I have had numerous enlightening discussions with John about semiclassical physics.

I also want to thank Pam Leland, who was helpful in proofreading the final manuscript.

This research was completed through a grant from the Department of Energy, Office of Basic Energy Sciences.

# Contents

## Chapter

<b>1</b>	Introduction	1
1.1	Historical background . . . . .	3
1.2	Outline of the results . . . . .	10
1.3	Scaled variable recurrence spectroscopy . . . . .	12
<b>2</b>	Time independent scattering matrices and quantization	15
2.1	Quantum defect theory . . . . .	16
2.1.1	Energy normalized Coulomb functions . . . . .	17
2.1.2	Channel functions . . . . .	18
2.1.3	$S$ -matrices in quantum-defect theory . . . . .	19
2.2	$S$ -matrices for atoms in external fields . . . . .	22
2.2.1	$S$ -matrix states . . . . .	25
2.2.2	Quantization using $S$ -matrices . . . . .	26
2.2.3	Normalization . . . . .	30
2.3	Discussion . . . . .	32
<b>3</b>	Coarse grained photoabsorption spectra	35
3.1	Preconvolved quantum-defect theory . . . . .	36
3.1.1	Energy smoothing of the cross section . . . . .	38
3.1.2	Finding the Green's function . . . . .	39

3.1.3	Putting it all together . . . . .	43
3.2	Interpretation and discussion . . . . .	45
3.2.1	Expansion of the cross section . . . . .	45
3.2.2	Semiclassical approximations . . . . .	49
3.2.3	Conclusion . . . . .	52
<b>4</b>	<b>Quantum scattering matrices</b>	<b>53</b>
4.1	Variational $S$ -matrix approach . . . . .	56
4.1.1	Solving the Schrödinger equation . . . . .	56
4.1.2	Finding the $S$ -matrix . . . . .	62
4.1.3	Scaled variable $S$ -matrices . . . . .	66
4.2	Recurrences in the quantum $S$ -matrix . . . . .	66
<b>5</b>	<b>Semiclassical <math>S</math>-matrices</b>	<b>73</b>
5.1	The $S$ -matrix and the Green's function: an exact relationship . . . . .	75
5.2	Surface projections of the Green's function by the method of stationary phase . . . . .	78
5.2.1	Initial angle projection . . . . .	82
5.2.2	Final angle projection . . . . .	84
5.3	Special cases and improvements . . . . .	88
5.3.1	Parallel orbit . . . . .	89
5.3.2	High angular momentum . . . . .	92
5.3.3	Bifurcations . . . . .	95
5.4	Results . . . . .	100
<b>6</b>	<b>Ghost orbits and core scattering</b>	<b>104</b>
6.1	Primitive semiclassical approximation . . . . .	106
6.2	Cancellation between ghost orbits and core scattered orbits . . . . .	109
6.2.1	Observation in the quantum recurrence spectra . . . . .	110

6.2.2	Observation in the shapes of the classical orbits . . . . .	114
6.2.3	Unanswered questions . . . . .	117
6.3	Resummed semiclassical cross section . . . . .	118
6.3.1	General approach . . . . .	118
6.3.2	Application to diamagnetic hydrogen . . . . .	124
6.3.3	Diamagnetic lithium-like atom . . . . .	124
6.3.4	Diamagnetic rubidium atom . . . . .	130
6.4	Conclusion . . . . .	137
<b>Bibliography</b>		139
<b>Appendix</b>		
A	Scaled variables for diamagnetic hydrogen	144
B	A survey of classical closed orbits in diamagnetic hydrogen	148
C	Semiclassical Green's function amplitude	153
D	Related publications	155

## List of Figures

### Figure

2.1	The various regions of configuration space in which a Rydberg electron in external electromagnetic fields travels are shown. . . . .	23
3.1	The theoretical and experimental photoabsorption spectra are shown for deuterium Rydberg atoms in an external magnetic field of 5.96 Tesla. . . . .	46
3.2	The convolved photoabsorption cross section is plotted for $m = 0$ , even parity states of hydrogen in a 5.96 Tesla field. . . . .	47
4.1	This diagram depicts the volume $V$ of configuration space in which the Schrödinger equation must be solved to find the long-range $S$ -matrix. . . . .	57
4.2	The real (bottom) and imaginary (top) parts of the regular (solid line) and irregular (dotted line) Coulomb functions ( $f, g$ ) are plotted at a complex energy $E = -0.0005 + 0.5 \times 10^{-6}i$ and angular momentum $l = 1$ . . . . .	64
4.3	The real part of an element of $\underline{S}^{\text{LR}}$ is shown as a function of the scaled field $w$ . . . . .	68
4.4	The Fourier transforms or recurrence strengths ( $R(\tilde{S})$ , Eq. (4.27)) of individual elements of the long range $S$ -matrix are shown. . . . .	69
4.5	Recurrence strengths of the matrix element $Re(S_{44}^{\text{LR}}(w))$ are plotted for multiple scaled energies. . . . .	71
5.1	The classical scaled action $\tilde{S}(\theta_f)$ is given as a function of the final angle $\theta_f$ for trajectories returning to a sphere of scaled radius $\tilde{r}_0 = 0.1$ . . . . .	99

5.2	A comparison is shown between the quantum (upright) and semiclassical (inverted) recurrence strengths $R(\tilde{S})$ of elements of $\underline{S}^{\text{LR}}$ . . . . .	101
5.3	A comparison is shown of quantum (upright) and semiclassical (inverted) recurrence strengths for odd parity, $m = 0$ , elements of the long-range $S$ -matrix. . . . .	102
6.1	A comparison is shown between the accurate quantum (upright) and primitive semiclassical (inverted) recurrence strength for diamagnetic hydrogen at a scaled energy of $\epsilon = -0.3$ . . . . .	108
6.2	The Fourier transform, or recurrence strength, of the preconvolved photoabsorption cross section $\sigma(w)$ for diamagnetic hydrogen is given at seven scaled energies ( $\epsilon = -0.9 \rightarrow -0.3$ ). . . . .	112
6.3	The recurrence strength of the linear term in the expansion of the photoabsorption cross section $2\text{Re}d\vec{S}^{\text{LR}}(w)\vec{d}^\dagger$ is plotted, again for diamagnetic hydrogen (even parity, $m = 0$ ) at the seven scaled energies shown in Fig. 6.2. . . . .	113
6.4	The recurrence strength of the quadratic term in the expansion of the photoabsorption cross section $2\text{Re}d\vec{S}^{\text{LR}}(w)^2\vec{d}^\dagger$ is plotted, again for diamagnetic hydrogen (even parity, $m = 0$ ) at the seven scaled energies shown in Figs. 6.2 and 6.3. . . . .	115
6.5	This figure shows the topological similarity between the ghost orbits (left) and the core-scattered orbits (right). . . . .	116
6.6	The quantum (upright) and semiclassical (inverted) recurrence spectra for diamagnetic hydrogen is plotted at three scaled energies ( $\epsilon = -0.7, -0.5, -0.3$ ). . . . .	125
6.7	The photoabsorption cross section $\sigma(w)$ for diamagnetic hydrogen is shown at a scaled energy $\epsilon = -0.3$ as a function of the scaled field $w$ . . . . .	126
6.8	The semiclassical cross section $\sigma(w)$ , Eq. (6.17), is shown along with the convergence factor $\kappa$ , Eq. (6.20), for a lithium-like atom ( $\mu_s = 0.4$ ) over the range $w = 100 - 500$ . . . . .	127

6.9	A comparison is shown between the improved semiclassical (inverted) cross section, Eq. (6.19), and an accurate quantum calculation for $m = 0$ , even parity final states of a lithium-like atom ( $\mu_s = 0.4$ ). . . . .	128
6.10	The quantum (upright) and semiclassical (inverted) recurrence strength for H and Li of the total photoabsorption cross section $\sigma(w)$ is shown at a scaled energy of $\epsilon = -0.3$ . (a) Diamagnetic hydrogen recurrence spectra for $m = 0$ , even parity final states ( $\Delta w = 0.6, w = 100 - 500$ ). . . . .	129
6.11	The scaled variable photoabsorption cross section $\sigma(w)$ is shown for $m = 0$ , even parity states of a diamagnetic rubidium-like atom ( $\mu_s = 3.13, \mu_d = 1.34$ ). . . . .	131
6.12	The quantum (upright) and semiclassical (inverted) recurrence strength is given of the scaled photoabsorption spectrum shown in Fig. 6.11. . . . .	132
6.13	The scaled variable photoabsorption cross section $\sigma(w)$ of diamagnetic rubidium is plotted at a scaled energy of $\epsilon = -0.3$ ( $m = 0$ , even parity). . . . .	133
6.14	The recurrence strength of the scaled variable cross section $\sigma(w)$ shown in Fig. 6.13 is plotted. . . . .	134
6.15	A resummed semiclassical calculation is given for rubidium at a relatively high value of $w = 2100 - 2500$ , where no quantum calculations are available. . . . .	135
A.1	The fraction of classical phase space that is regular for diamagnetic hydrogen is plotted as a function of the scaled energy $\epsilon = EB^{-2/3}$ . . . . .	146
B.1	The scaled actions $\tilde{S}$ of classical closed orbits of diamagnetic hydrogen are plotted versus the scaled energy $\epsilon$ . . . . .	151
B.2	The first 20 closed orbits of diamagnetic hydrogen are shown at a scaled energy of $\epsilon = -0.3$ . . . . .	152