

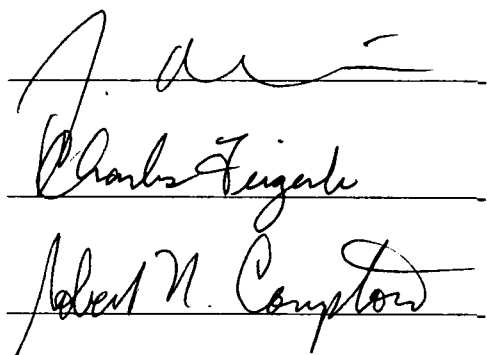
To the Graduate Council:

I am submitting herewith a dissertation written by Ivan L. Cordrey entitled "A Theoretical Study of Cooper Minima in Rydberg Atoms." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.



Joseph H. Macek, Major Professor

We have read this dissertation
and recom end its acceptance:



Accepted for the Council:



Associate Vice Chancellor and
Dean of The Graduate School

A THEORETICAL STUDY OF COOPER MINIMA IN RYDBERG ATOMS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
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Ivan L. Cordrey
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DEDICATION

This dissertation is dedicated to my wife

Susan H. Ford

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ABSTRACT

This theoretical study investigates the parameters that affect the location of Cooper minima in photo-excitation spectra of Rydberg atoms. The bound-bound and bound-free transitions are examined. In this study, the wave functions used are obtained from Schwinger's variational principle for a central screened Coulomb potential. These Schwinger wave functions are analytic integral representations which depend explicitly on the quantum defect μ (or the phase shift δ for continuum states). The radial dipole matrix elements are evaluated analytically and reduce to one contour integral on finite limits that is easily evaluated by standard numerical techniques. The wave functions compare favorably with Hartree-Fock wave functions, and the dipole matrix elements compare favorably with experimental results. The energy E_{CM} of the final state for which a Cooper minimum occurs is studied as a function of the difference in quantum defect $\Delta\mu = \mu_f - \mu_i$ of the initial and final states. It is shown that the major determiner of E_{CM} is $\Delta\mu$, while the absolute quantum defects μ of initial and final states are minor corrections. It is seen that the occurrence of Cooper minima is qualitatively similar for all $l \rightarrow l + 1$ transitions. Likewise, the Cooper minima of all $l \rightarrow l - 1$ transitions are also qualitatively similar. However the trends in Cooper minima are qualitatively different for $l \rightarrow l + 1$ transitions compared to $l \rightarrow l - 1$ transitions. It is seen that Cooper minima that occur far from the ionization threshold are independent of the initial state principle quantum number (*i.e.* initial state energy), while Cooper minima that occur close to threshold are shifted to higher energy as the initial state principle quantum number is increased. Results compare favorably with Hartree-Fock calculations and limited experimental evidence.

Contents

1	Introduction	1
2	Theory	9
2.1	Theoretical Background	9
2.2	The Radial Wave Function	14
2.2.1	A review of Schwinger's variational principle	15
2.2.2	Free state wave function	17
2.2.3	Bound state wave function	19
2.2.4	Functional forms	19
2.2.5	Similarity to hydrogen wave functions	21
2.2.6	Application	24
2.3	Radial Dipole Matrix	30
3	Results and Discussion	37
3.1	General Studies of Cooper Minima	37
3.1.1	Movement of Cooper minima with changes in $\Delta\mu$	37
3.1.2	Explicit dependence on μ	44
3.1.3	Dependence on nuclear charge Z	46
3.1.4	Dependence on variable δ	47

3.2	Studies of Rydberg Atom Cooper Minima	49
3.2.1	Movement of the Cooper minima for different n_i	49
3.2.2	Conditions for very near threshold Cooper minima for high Rydberg states	53
3.3	Applications and comparisons with other works	58
4	Conclusions	66
	Bibliography	70
	Appendices	75
A.	A derivation of $\langle \vec{r} G_l V F_l \rangle$	76
B.	Continuity of the wave functions across threshold	81
C.	A list of matrix elements	84
D.	Evaluation of R	87
D.0.1	Evaluation of R for bound-continuum transitions	87
D.0.2	Evaluation of R for bound-bound transitions	93
	Vita	94

List of Figures

1-1	The photo excitation cross section of various atoms showing examples of Cooper minima.	4
2-1	The integration contour for $G_l V F_l\rangle$	20
2-2	The integration contour for the hydrogen-like $G_l V F_l\rangle$	22
2-3	The Li(2s) wave function comparison.	25
2-4	The Schwinger wave functions of the Li(ns) Rydberg series.	27
2-5	A comparison of two $n = 5$ wave functions with the same quantum defect $\mu = 0.42$ but different nuclear charges $Z = 3$ and $Z = 11$	29
2-6	The relationship between Cooper minima in the cross section and the zero of the radial dipole matrix element.	34
2-7	The oscillator strength spectrum for the bound-bound and bound-continuum transitions of the Li(2s) state.	35
3-1	The migration of the Cooper minimum with changes in $\Delta\mu$ for $l \rightarrow l + 1$ transitions.	39
3-2	A continuation of the migration of the Cooper minimum with changes in $\Delta\mu$ for $l \rightarrow l + 1$ transitions.	40
3-3	The energy E_{CM} of the Cooper minimum as a function of $\Delta\mu = \mu_f - \mu_i$ for $l \rightarrow l + 1$ transitions.	40

3-4	The cross sections of $n = 5, l = 1 \rightarrow E, l' = 0$ showing the migration of the Cooper minima for different $\Delta\mu$	42
3-5	The energy E_{CM} of Cooper minimum as a function of $\Delta\mu$ for $l \rightarrow l-1$ transitions.	43
3-6	Direct dependence of the Cooper minimum on μ_i and μ_f	45
3-7	The energy E_{CM} of the Cooper minimum as a function of threshold $\Delta\mu$	48
3-8	The intersection of $\delta_f(E)/\pi = \Delta\mu(E)$ and $\Delta\mu_f(E_{CM})$ predicting a Cooper minimum.	49
3-9	The energy E_{CM} of the Cooper minimum as a function of $\Delta\mu$ for $l \rightarrow l + 1$ transitions and different initial state principle quantum number.	50
3-10	The energy E_{CM} of the Cooper minimum as a function of $\Delta\mu$ for $l \rightarrow l - 1$ transitions and different initial state principle quantum number.	52
3-11	The $\Delta\mu$ necessary for a Cooper minimum at threshold as a function of $1/n_i$ for $l \rightarrow l + 1$ transitions.	54
3-12	The $\Delta\mu$ necessary for a Cooper minimum at $E_{CM} = 0.01\text{Ry}$ as a function of $1/n_i$ for $l \rightarrow l - 1$ transitions.	56
3-13	A comparison of the $\Delta\mu$ necessary for a Cooper minimum at $E_{CM} = 0.01\text{Ry}$ and $E_{CM} = 0.0025\text{Ry}$ as a function of $1/n_i$ for $l = 2 \rightarrow 1$ transitions.	57
3-14	A comparison of photoionization cross sections for the lithium Rydberg series of initial states.	59
3-15	The bound-bound and bound-free photo-excitation cross sections for a sample of the lithium Rydberg series initial states.	61

3-16	The bound-free photo-excitation cross sections for sodium $4d \rightarrow \varepsilon p$ transitions.	64
A-1	The integration contour for $G_l V F_l\rangle$	80

Chapter 1

Introduction

Photoabsorption is the physical process whereby an atom, ion or molecule absorbs electromagnetic radiation (*i.e.* light) causing an electron to move from a lower energy bound state to a higher energy bound state. If the energy absorbed from the radiation field by the electron is greater than the ionization limit for that electron, the electron enters a continuous, positive energy free state; *i.e.* the atom is ionized and this process is called photoionization. These processes of photo-absorption and -ionization are important in the study of atmospheric science (especially in the upper atmosphere), astrophysics (*e.g.* the atomic/molecular “signature” in the light from interstellar gas clouds, stars, etc.), plasma physics (as a fundamental process and as a plasma diagnostic tool), and is of fundamental importance as a probe of atomic properties. Given that the primary physical difference between the processes of photoabsorption and photoionization is whether the final state’s energy is below or above the ionization threshold, these two processes are essentially very similar. Consequently the term “photo-excitation” will be used throughout this work to refer to photoabsorption and photoionization collectively.

In the study of photo-excitation there is actually only one class of atomic sys-

tems that are “completely” solved; that is the hydrogen atom and other one electron hydrogen-like ions. For the simple case of hydrogen’s one electron around a bare nuclear charge, the exact electron wave functions for bound states and free electron states, as well as expressions for the transition matrix elements from one state to another, were determined in closed form by Gordon in 1929[1].

For all other multi-electron atomic systems no exact closed form expressions for either the wave functions or transition matrix elements are known. For these atoms much work has been done to find good approximate methods to calculate wave functions and matrix elements. The best approximations rely on a computer to solve the multi-electron Schrödinger equation in some form. Some of the more successful theories are R-matrix[2], and Hartree-Fock/Dirac-Fock[3]. These computational methods can give numerical results that are quite accurate.

The photo-excitation cross section is proportional to the square of the transition matrix element and is a measure of the probability of photo-excitation for a given incident photon energy. In the case of hydrogenic systems, the photo-excitation cross sections are monotonically decreasing with increasing final state energy. But for multi-electron atoms this may not be the case. A Cooper minimum[4, 5] is a minimum in the photo-excitation spectrum that occurs because the transition matrix passes through zero as it changes sign from positive to negative or from negative to positive. Since the transition matrix is squared to give the physically measured cross section, a spectrum of cross sections that shows a single Cooper minimum will decrease to near zero (the Cooper minimum), then rise to a secondary maximum and finally decrease monotonically with increasing final state energy. Such a Cooper minimum can have a large impact on the photo-excitation spectrum when it occurs in the bound-bound or near threshold bound-free transitions.

The classic examples of Cooper minima are the photo-excitation spectra of the va-

lence electron of ground state alkali metals: lithium, sodium, and potassium. Shown in Figure 1-1 are the photo-excitation cross sections for hydrogen 1s (calculated), lithium 2s (experimental[6, 7]), and sodium 3s (experimental[7, 8]) plotted as a function of final state energy E . There is no Cooper minimum for hydrogen, while a Cooper minimum occurs in the bound-bound transitions of lithium at about -2eV, and in the near threshold bound-free transitions of sodium. It is clearly seen that the presence of a Cooper minimum in the photo-excitation spectrum leads to spectra that deviate sharply from the hydrogenic model.

Such Cooper minima do not occur in the dipole matrix elements of hydrogen[9], but Cooper minima can occur in almost any other atomic system; for example, multi-electron atoms[10] and positive ions[11], negative ions[12], molecules[13], and even solid state matter[14]. Because of the wide spread occurrence of Cooper minima it is seen that the hydrogenic case is in fact a special case because of its lack of minima (although minima do appear in the hydrogenic multipole transitions[15]).

This research focuses on Cooper minima of Rydberg atoms. A Rydberg atom is a neutral atom with its outer most valence electron in a state with principle quantum number n much higher than its normal ground state, while the rest of the electrons are in the ground state close to the nucleus. An electron in such a high n -state is called a Rydberg electron and is spatially and energetically separated from the other electrons called the core. Because of this separation, the potential experienced by the Rydberg electron is nearly hydrogenic except near the core. Thus Rydberg atoms are the simplest atomic systems after the hydrogenic systems. Indeed the major characterization of a Rydberg state is its quantum defect μ . The quantum defect μ describes the energy shift of the Rydberg state relative to the corresponding hydrogen state. The quantum defect is also related to the phase shift of the Rydberg state's wave function relative to the corresponding hydrogenic wave function. In fact, according to

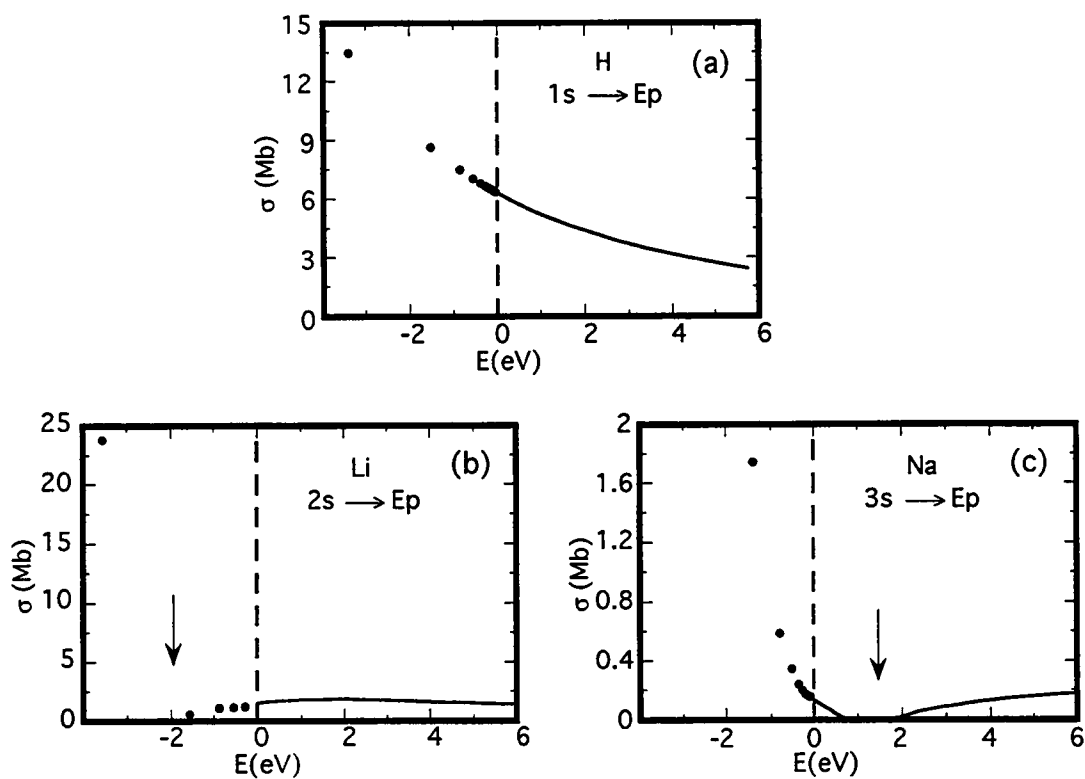


Figure 1-1: The photo excitation cross section of various atoms showing examples of Cooper minima. (a) Hydrogen 1s state shows no minimum, (b) Lithium 2s state (experiment[6, 7]) shows a minimum at about -2eV, (c) Sodium 3s state (experiment[7, 8]) shows a minimum at about 1.5 eV. The horizontal axis is the final state energy E . The arrow points out the approximate location of the Cooper minimum in these cases.

quantum defect theory[16], the quantum defect multiplied by π continues smoothly across the ionization threshold to become the phase shift δ of the continuum state's wave function compared to the hydrogen wave function of the same energy. This statement from quantum defect theory is embodied in the equation

$$\lim_{E_n \rightarrow 0^-} \pi\mu = \lim_{\varepsilon \rightarrow 0^+} \delta(\varepsilon) , \quad (1.1)$$

where E_n is the binding energy of the n 'th Rydberg state, and ε is the energy of the continuum state. Equation 1.1 shows the natural connection between high Rydberg states and the continuum states. Because of this natural connection between Rydberg states and the continuum it is desirable to have a theory that can treat the entire Rydberg series of states and the continuum states as a unit. Although it is true that there are other aspects of being part of a multi-electron atom that affect Rydberg states such as electron exchange, but such effects are not treated in this study. Of course, a study of Cooper minima in Rydberg atoms must first include an understanding of Cooper minima generally, so this work also extensively studies Cooper minima in general. Although there is a large volume of work on Cooper minima in the literature, it does not create a coherent study of Cooper minima. Thus the general studies of Cooper minima in this work are also quite useful.

There have been some theoretical studies of Cooper minima in the photoionization of excited states of cesium[17, 18], sodium[19, 20], and nitrogen[21], and more recently of lithium[22]. These works used numerical wave functions from Hartree-Fock/Hartree-Slater computer codes. There are even more sophisticated numerical calculations that use the random-phase approximation and Dirac-Fock method[23, 24]. What is seen from these works is that with sufficient computer power, time and effort, the experimental data[25, 26, 27, 28, 29] can eventually be modeled to apparently good accuracy; however, many predictions of Cooper minima have been difficult to prove experimentally. The theoretical works referenced above also show that the

quality of the wave function is essential to accurate predictions of the location of Cooper minima. As will be seen in section 2.2, the semi-empirical wave functions of the Bates-Damgaard approximation[30] are not of sufficient quality to give reasonable predictions of Cooper minima. There is also one theoretical survey focused on the multiple Cooper minima of excited d-states for higher nuclear charges[31], but there has been no survey of Cooper minima in Rydberg atom's that studies the trends along an atom's Rydberg series with increasing initial principle quantum number n_i .

Considering that the major characteristic of Rydberg states is the quantum defect, it is useful to study the systematics of Cooper minima with a simple theory that treats the quantum defect in a non-trivial manner, but includes little else. Such a treatment should provide insight into what aspects of Cooper minima are due to quantum defects (phase shifts), and what aspects require more detailed treatments. There has already been some work relating quantum defects to Cooper minima[32], but the work was not a thorough survey of Cooper minima of Rydberg states.

The first step in this simple theory of photo-excitation of Rydberg atoms is to obtain analytic wave functions that include the quantum defect in a readily accessible form. The wave functions used in this work are obtained from Schwinger's variational principle using a screened Coulomb potential as discussed by Maleki[33, 34]. The use of a screened Coulomb potential does not include effects such as electron exchange and core polarization; yet, local potentials are often used to model Rydberg atoms. The use of Schwinger's variational principle has been extensively studied, and Watson[35] has developed the Schwinger method into a general numerical method that is fully *ab initio*. These calculations by Watson use more sophisticated potentials and wave functions, both of which must be obtained numerically, but the theory in such cases is essentially exact. The simple form of the wave functions used in this present study of Rydberg atoms thus constitutes a simple approximation to an exact theory. The wave

functions used in the present study have a relatively simple analytic form that in some ways resembles the hydrogenic wave functions in integral representation. This theory also treats the bound and continuum states as a unit, with wave functions that are automatically orthonormal and analytically continue across the ionization threshold. These wave functions depend explicitly on the nuclear charge Z , and the quantum defect μ . The only fitting parameter is the quantum defect $\mu(0)$ at threshold which is variationally adjusted to match the experimental quantum defect at threshold. An important limitation of this theory is that when only one Slater-type orbital is used as the variational function (as it is for simplicity in this study) the quantum defect can only be in a range $0 \leq \mu \leq 1$. It was shown by direct calculation that this restriction on μ does not apply when two or more Slater orbitals are used[34].

The calculation of the radial dipole matrix in this work reduces to an analytic form involving one contour integral with finite limits that can be easily evaluated by numerical integration. The net result is that by fitting the threshold phase shift with the parameter (r_c) the dipole matrix elements for the entire Rydberg series and the continuum can be calculated quickly and easily. The results are numerically stable except for a small energy region around the ionization threshold of about $\pm 0.01\text{eV}$ in most cases, but since the Rydberg series below this region and the continuum above this region are easily calculated, the threshold values can be interpolated.

The theory used in this work is discussed in Chapter 2. The fundamental results from quantum mechanics necessary for the study of Cooper minima are reviewed briefly in section 2.1. The Schwinger wave functions used in this study are introduced and discussed in section 2.2. The wave functions are shown to be very similar in functional form to the hydrogen wave functions. The Schwinger wave function for lithium 2s is compared to the Hartree-Slater wave function, and quantum defects are compared to experimentally determined values. Section 2.3 gives explicit expressions

for the radial dipole matrix elements using Schwinger wave functions, and calculations for lithium 2s photo-excitation are compared to experimental results.

Chapter 3 contains the studies of Cooper minima. In section 3.1 the general systematics of Cooper minima are studied and discussed mainly as a function of the quantum defect difference $\Delta\mu = \mu_f - \mu_i$ of the initial and final states of the transition. Both $l \rightarrow l + 1$ transitions and $l \rightarrow l - 1$ transitions are examined and the general trends of the energy at which Cooper minima occur are illuminated. The explicit studies of Cooper minima in Rydberg atoms are contained in section 3.2, where the systematics of the Cooper minima for entire Rydberg series of initial states are presented and discussed. Here again both $l \rightarrow l + 1$ and $l \rightarrow l - 1$ transitions are treated. The knowledge gained from these theoretical studies of Cooper minima are applied to a few real physical systems in section 3.3 where the Schwinger calculations are compared to other available calculations and experimental evidence of Cooper minima.

Chapter 4 summarizes this work and draws general conclusions. And the Appendices contain the detailed mathematical derivations of the wave functions, and aspects of the radial dipole matrix expressions.

Atomic units[36] are used throughout except where explicitly noted otherwise.

Chapter 2

Theory

2.1 Theoretical Background

The study of Cooper minima requires a basic understanding of photon-atom interactions. To this end, it is necessary to first review the basic theory, and this section covers only the relevant major results of photon-atom interactions. For a more comprehensive view of photon-atom interactions see a standard reference[3].

When an atom is impinged by electro-magnetic radiation, an electron in the atom can absorb energy from the radiation field causing the electron to change its quantum state. This change of state is called a transition, and in the case of photo-excitation, the transition is from a lower energy state to a higher energy state. Assuming that the intensity of the radiation field is low and the energy of the light is below $\hbar\nu \sim 10$ keV, the transition is governed by the electric dipole approximation which is used throughout this work.

The physically measured quantity in a photo-excitation experiment is the cross section σ . The cross section is proportional to the probability that an atom will absorb a photon causing an electron in the atom to make a transition from an initial state of

energy E_i to a final state of energy E . The energy $\hbar\nu$ of the photon absorbed is equal to the change in energy of the electron: $\hbar\nu = E - E_i$. In the equations that follow, the notation used is an effort to present the bound-bound and bound-free transitions in a unified context. When bound-bound transitions are treated it is important to realize that $E = E_{n_f, l_f}$, and that although the equations are written with E as a continuous variable, E of the a bound state is a discrete variable. The cross section is given by

$$\sigma(E) = 4\pi^2\alpha(E - E_i)|\vec{\pi}_\lambda \cdot \vec{r}_{fi}|^2 \quad (2.1)$$

where $\alpha \simeq 1/137$ is the dimensionless fine structure constant, E_i is the fixed energy of the initial state, E is the energy of the final state, $\vec{\pi}_\lambda$ is the polarization of the photon, and $\vec{r}_{fi}$ is the dipole matrix element given by

$$\vec{r}_{fi} = \langle \Psi_f^E | \vec{r} | \Psi_i \rangle \quad (2.2)$$

where Ψ_f^E and Ψ_i are the full wave functions of the final and initial state respectively. Note that the cross section of Eq. (2.1) has units of area, so in this formulation one of the wave functions Ψ_f^E in Eq. (2.2) is normalized to unit energy (hence the E superscript). For continuum states it is standard to normalize to unit energy, so in bound-free transitions the Ψ_f^E is already normalized appropriately. In the case of bound-bound transitions it is necessary to renormalize Ψ_f to unit energy; this is accomplished by multiplying the wave function by the factor $(n_f - \mu_f)^{3/2}$. With this factor the cross section for a bound-bound transition in terms of wave functions normalized to unity is defined by

$$\sigma_{n_i l_i, n_f l_f}(E) = 4\pi^2\alpha(E - E_i)(n_f - \mu_f)^3 |\vec{\pi}_\lambda \cdot \vec{r}_{fi}|^2 \delta(E - E_{n_f l_f}) . \quad (2.3)$$

where the $\delta(E - E_{n_f l_f})$ is the Dirac delta function that ensures that the cross section $\sigma_{n_i l_i, n_f l_f}(E)$ is zero everywhere except at the discrete energies $E_{n_f l_f}$ of available bound final states.

In the independent-electron model with a central potential (like a screened Coulomb potential) it is convenient to describe the wave functions in polar coordinates. This allows a convenient separation of the wave function into radial and angular parts:

$$\Psi(\vec{r}) = \frac{P(r)}{r} Y_{l,m}(\theta, \phi) . \quad (2.4)$$

Here the $Y_{l,m}(\theta, \phi)$ are the familiar spherical harmonic functions, and l and m are the standard good quantum numbers known from the hydrogenic wave functions. With this separation of variables one can evaluate the angular integrals in $\vec{r}_{fi}$ of Eq. (2.2) which gives the usual dipole transition selection rules

$$\Delta l = l_f - l_i = \pm 1 , \quad \Delta m = m_f - m_i = 0, \pm 1 \quad (2.5)$$

and contributes the numerical factor

$$F(l_f, l_i) = \begin{cases} \sqrt{l_f/(2l_f + 1)} & \text{for } l_f = l_i + 1 , \\ -\sqrt{l_i/(2l_f + 1)} & \text{for } l_f = l_i - 1 . \end{cases}$$

And since the m states of initial l_i multiplet and final l_f multiplet are seldom distinguished in experiments, it is convenient to average over the initial m_i states and sum over the final m_f . Thus the cross section becomes

$$\sigma(E) = \frac{4\pi^2\alpha (E - E_i)}{3(2l_i + 1)} \left\{ l[R_{l-1}(E)]^2 + (l+1)[R_{l+1}(E)]^2 \right\} , \quad (2.6)$$

where $R_{l\pm 1}(E)$ is the radial dipole matrix element given by

$$R_{l\pm 1}(E) = \langle P_{f,l\pm 1}(r, E) | r | P_{i,l}(r) \rangle = \int_0^\infty dr P_{f,l\pm 1}(r, E) r P_{i,l}(r) , \quad (2.7)$$

where E is the final state energy. This is called the “length” form of the radial dipole matrix element. Using commutation relations R can be cast in a different form called the “velocity” form [see Ref. [5] for details of these two forms]. It is known[36] that the evaluation of R in length form has its largest contribution from large radius, while the evaluation of R in velocity form has its largest contribution from smaller

radius. It has been suggested by other researchers[19] that the velocity form of the radial dipole matrix element is a computationally more reliable form of the dipole matrix. The velocity form is apparently more reliable in the case of numerical wave functions where the asymptotic region is less accurate than the inner region. The velocity form the radial integral converges more quickly at smaller radius making it computationally easier to evaluate accurately the velocity form than the length form when numerical wave functions are used. In the case of the theory presented in this work, the wave functions are analytic and the asymptotic regions are well known (and more reliable than the inner region) [see section 2.2]. Moreover, the integral over r $(0, \infty)$ is evaluated analytically [see section 2.3] so there is no computational difficulty associated with the use of the length form of R given by Eq. (2.7). Thus the concerns expressed elsewhere about the length form of the radial dipole matrix do not apply in the unique case of this study where most everything is done analytically.

In photo-excitation work it is common to define a unitless quantity for bound-bound transitions called the oscillator strength that is defined as

$$f_{n_f l_f, n_i l_i} = \frac{2}{3} (E_{n_f l_f} - E_{n_i l_i}) \frac{l_{>}}{2l_i + 1} [R_{n_f l_f}]^2 \quad (2.8)$$

where $l_{>}$ is the larger of l_f and l_i . For bound-continuum transitions from the bound state n_i, l_i to the continuum state E, l_f one has the corresponding quantity called the spectral density of oscillator strength

$$\frac{f_{E l_f, n_i l_i}}{dE} = \frac{2}{3} (E - E_{n_i l_i}) \frac{l_{>}}{2l_i + 1} [R_{l_f}(E)]^2 \quad (2.9)$$

because the continuum state is energy normalized. One can also define the oscillator strength density $\frac{df_{n_f l_f, n_i l_i}}{dE}$ for a bound-bound transition that continues smoothly across the ionization threshold to become $\frac{f_{E l_f, n_i l_i}}{dE}$ for the bound-continuum transition. This bound-bound spectral oscillator strength density requires that the final bound state wave function be energy normalized. The energy normalization factor $(n_f - \mu_f)^{3/2}$ for

the final bound state wave function can be factored out of $[R]^2$, thus the oscillator strength density for bound-bound transitions is defined by

$$\frac{df_{n_f l_f, n_i l_i}}{dE} = \frac{2}{3}(E - E_{n_i l_i})(n_f - \mu_f)^3 \frac{l_i}{2l_i + 1} [R_{l_f}(E)]^2 \delta(E - E_{n_f l_f}). \quad (2.10)$$

where the $\delta(E - E_{n_f l_f})$ denotes that although written as a continuous function of final state energy E , Eq. (2.10) is only defined at the physical energies $E_{n_f l_f}$ of the final bound states. When dealing with a local potential (*i.e.* ignoring electron exchange) the total of all oscillator strengths for transitions from state $(n_i l_i)$ obeys the sum rule

$$\sum_{n_f l_f} f_{n_f l_f, n_i l_i} + \int_0^\infty \frac{f_{E l_f, n_i l_i}}{dE} dE = 1. \quad (2.11)$$

where the sum/integral includes both the $l_f = l_i + 1$ and $l_f = l_i - 1$ channels, and $E = 0$ is taken as the ionization threshold. This sum rule can also be split into contributions from the individual channels

$$\begin{aligned} \sum_{n_f l_i+1} f_{n_f l_i+1, n_i l_i} + \int_0^\infty \frac{f_{E l_i+1, n_i l_i}}{dE} dE &= \frac{1}{3} \frac{(l_i + 1)(2l_i + 3)}{2l_i + 1}, \\ \sum_{n_f l_i-1} f_{n_f l_i-1, n_i l_i} + \int_0^\infty \frac{f_{E l_i-1, n_i l_i}}{dE} dE &= -\frac{1}{3} \frac{l_i(2l_i - 1)}{2l_i + 1}. \end{aligned} \quad (2.12)$$

The cross section of Eq. (2.6) can be expressed in terms of the oscillator strength density as

$$\begin{aligned} \sigma(E) &= 2\pi^2 \alpha \left\{ \frac{f_{E l_i-1, n_i l_i}}{dE} + \frac{f_{E l_i+1, n_i l_i}}{dE} \right\} \\ &= 1.098 \times 10^{-16} \text{cm}^2 \text{ eV} \left\{ \frac{f_{E l_i-1, n_i l_i}}{dE} + \frac{f_{E l_i+1, n_i l_i}}{dE} \right\} \end{aligned} \quad (2.13)$$

One can also discuss the cross section of a single l_f channel, like the $l_f = l_i + 1$ channel.

$$\begin{aligned} \sigma_{l+1}(E) &= 2\pi^2 \alpha \frac{f_{E l_i+1, n_i l_i}}{dE} \\ &= \frac{4}{3} \pi^2 \alpha (E - E_{n_i l_i}) \frac{l_i + 1}{2l_i + 1} [R_{l_i+1}^E(E)]^2, \end{aligned} \quad (2.14)$$

or in cgs-units

$$\sigma_{l+1}(E) = 1.098 \times 10^{-18} \text{cm}^2 \text{ eV} \frac{f_{E l_i+1, n_i l}}{dE} \quad (2.15)$$

where $\frac{df}{dE}$ is in units of eV^{-1} . Looking at the single channel form of the cross section in Eq. (2.14), one can see that if the radial dipole matrix R_{l+1} changed sign from positive to negative, *i.e.* passed through zero, at some energy E_{CM} that there would be a minimum in the cross section spectrum at E_{CM} . Minima of this type are readily observed in the photo-excitation of ground state alkali atoms (Li, Na, K...) [see Figure 1-1] Such a minimum is termed a “Cooper minimum” because J. W. Cooper[4] was the first to recognize that such minima were a general phenomenon.

It is important to realize that the above discussion assumes that the atom in question has a low nuclear charge Z so that $l - s$ coupling is appropriate. For high Z atoms where $j - j$ coupling is appropriate, the relativistic effects split the initial state l -multiplet and the equations above would need to be modified. In such high Z cases the splitting of the initial state can “wash-out” the Cooper minimum because each state of the initial multiplet will have its Cooper minimum for a slightly different final state energy. In this work, $l - s$ coupling is assumed.

2.2 The Radial Wave Function

As stated above, in the independent-electron model a central screened potential preserves the angular quantum numbers l and m and the angular part of the wave function $Y_{l,m}(\theta, \phi)$ is the familiar spherical harmonic. Yet, the radial part of the wave function is still to be determined. For the purposes of a Rydberg electron around an inner core of electrons, the core potential can be approximated by

$$V = \frac{\lambda e^{-\sigma r}}{r} \quad (2.16)$$

where $\lambda = -(Z - 1)$, Z = the nuclear charge, and $1/c \sim$ "radius of the core". The full potential V_{full} would be the core potential plus the long range Coulomb potential: $V_{full} = V + \frac{1}{r}$.

The radial wave functions used in this work were derived by Maleki[33, 34] through use of Schwinger's variational principle.

2.2.1 A review of Schwinger's variational principle

Schwinger's variational principle for both free and bound states is discussed in works by Maleki[33, 34]. What follows is a very brief overview of Schwinger's variational principle used to derive wave functions.

Starting with the radial Schrödinger equation for a Rydberg electron

$$(h_l + V - \varepsilon)|F\rangle = 0 \quad (2.17)$$

where

$$h_l = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r} \quad (2.18)$$

is the hydrogen Hamiltonian, and V is a short range potential representing the non-hydrogenic core. Eq. (2.17) can be cast in the form of an inhomogeneous Schrödinger equation for hydrogen:

$$(h_l - \varepsilon)|F\rangle = -V|F\rangle. \quad (2.19)$$

Sugar and Blankenbecler[37] showed that Schwinger's variational principle can be derived from the radial Schrödinger equation Eq. (2.19) by replacing V with a separable potential

$$V^S = \frac{V|F_t\rangle\langle F_t|V}{\langle F_t|V|F_t\rangle} \quad (2.20)$$

where $|F_t\rangle$ is a variational trial function. Because V is a short range potential, $|F_t\rangle$ needs to a good approximation to the wave function only at small radius. This substitution leads to a solution of Eq. (2.17) of the form

$$|F^{(S)}\rangle = |f_l\rangle + G^{(P)}V|F_t\rangle C \quad (2.21)$$

where

$$G^{(P)} = f_l(r_<) g_l(r_>) \quad (2.22)$$

is the principle part Coulomb Green's function, and f_l is the regular Coulomb function while g_l is the irregular Coulomb function. It can be shown that the constant C is given by

$$C = \frac{\langle F_t|V|f_l\rangle}{\langle F_t|V - VG^{(P)}V|F_t\rangle} . \quad (2.23)$$

Examining the asymptotic limit of Eq. (2.21) yields

$$\lim_{r \rightarrow \infty} |F^{(S)}\rangle = \lim_{r \rightarrow \infty} |f_l\rangle + \lim_{r \rightarrow \infty} \{\langle f_l|V|F_t\rangle C\} \lim_{r \rightarrow \infty} |g_l\rangle \quad (2.24)$$

which compared to the standard limiting case of the solution to Eq. (2.17)

$$\lim_{r \rightarrow \infty} |F\rangle = \lim_{r \rightarrow \infty} |f_l\rangle + \tan \delta \lim_{r \rightarrow \infty} |g_l\rangle \quad (2.25)$$

gives Schwinger's variational expression for $\cot \delta$:

$$\cot \delta^{(S)} = \frac{\langle F_t|V - VG^{(P)}V|F_t\rangle}{|\langle F_t|V|f_l\rangle|^2} . \quad (2.26)$$

For continuum free states, the above expression for $\cot \delta^{(S)}$ is minimized variationally, which determines the parameters of the trial function $|F_t\rangle$ and thus the free state Schwinger wave function $|F^{(S)}\rangle$. In this study the variational parameter in $|F^{(S)}\rangle$ is a non-linear parameter, and the variation is done numerically at threshold.

This variational principle was extended to bound states by Maleki[33, 34]. For bound states, the exact solution of the Eq. (2.17) goes to zero asymptotically, so

$|F^{(S)}\rangle$ must also go to zero asymptotically. This asymptotic condition removes the homogeneous term $|f_l\rangle$ of Eq. (2.21), so the Schwinger bound state wave function is

$$|F_b^{(S)}\rangle = GV|F_t\rangle. \quad (2.27)$$

Since the bound states are discrete energy states, one must apply the following eigenvalue condition

$$\langle F_t|V - VG^{(P)}V|F_t\rangle = 0 \quad (2.28)$$

which determines the bound state energies, in addition to the variational condition. The quantum defect μ is determined by finding the bound state energy E_{nl} that solves Eq. (2.28), and applying

$$E_{nl} = \frac{1}{-2(n - \mu)^2}. \quad (2.29)$$

The wave functions given in Eqs. (2.21) and (2.27) are only approximate functions that depend on few parameters. As will be seen later they can give some very reasonable approximates to more sophisticated numerical wave functions.

2.2.2 Free state wave function

To apply the general Schwinger wave functions to photo-excitation one must ensure the proper normalization. The continuum state radial wave function of Eq. (2.21) normalized to unit energy takes the following form

$$|P_{\epsilon,l'}\rangle = \frac{\cos(\delta_{l'})}{\sqrt{\pi}} (|f_{l'}\rangle + G_{l'}^{(P)}V|F_{l'}\rangle C) \quad (2.30)$$

where C and $\cot(\delta_{l'})$ are given by Eqs. 2.23 and 2.26. Here $|f_{l'}\rangle$ is the regular Coulomb wave function

$$|f_{l'}\rangle = \frac{2^{l'+\frac{1}{2}}}{\Gamma(2l'+2)} k^{l'+\frac{1}{2}} \exp(-\pi\eta/2) |\Gamma(l'+1+i\eta)| e^{-ikr} r^{l'+1} \times {}_1F_1(l'+1-i\eta, 2l'+2, 2ikr) \quad (2.31)$$

$$\eta = -\frac{\gamma}{k} = -\frac{(Z-N)}{k} \quad (2.32)$$

where Z = nuclear charge, and N = number of core electrons; *i.e.* γ is the asymptotic charge of the residual ion after ionization. (Note: $|f_{l'}\rangle$ is normalized for use in Schwinger's variational principle, it differs from the standard normalization by $1/\sqrt{\pi}$). All the relevant matrix elements in C and $\cot(\delta_l)$ are evaluated explicitly in Appendix C. $G_{l'}^{(P)}$ is the principle value Coulomb Green's function given by

$$\begin{aligned} G_{l'}^{(P)} &= \frac{1}{2}(G_{l'}^+ + G_{l'}^-) \\ &= \frac{1}{2}(G_{l'}(X) + G_{l'}(-X)) \end{aligned} \quad (2.33)$$

where $X = -ik$. The last form is applicable because the potential V of Eq. (2.16), and the trial function $|F_l\rangle$ [see Eq. (2.37)] are both real functions. $G_{l'}^{(P)}$ is also given by

$$G_{l'}^{(P)} = G_{l'}(X) + i|f_{l'}\rangle\langle f_{l'}| \quad (2.34)$$

It has been found that a more useful form of Eq. (2.30) in terms of $G(-X)$ can be derived with Eqs. (2.33) and (2.34);

$$|P_{\epsilon, l'}\rangle = \frac{1}{\sqrt{\pi}} \left(e^{-i\delta_{l'}} |f_{l'}\rangle + \frac{\sin(\delta_{l'})}{\langle f_{l'}|V|F_{l'}\rangle} G_{l'}(-X)V|F_{l'}\rangle \right) \quad (2.35)$$

where $-X = +ik$. This form of $|P_{\epsilon, l'}\rangle$ leads to more readily accessible contour integrals when the radial dipole matrix element is evaluated.

It is important to note at this point that the free state wave function $|P_{\epsilon, l'}\rangle$ is a real function. This can be seen most readily from Eq. (2.30), where $|f_{l'}\rangle$ is a real function, and so is $G_{l'}^{(P)}V|F_l\rangle C$ because $|F_l\rangle$ and V are real functions and the principle value Green's function is used. Of course, the real function condition also exists for $|P_{\epsilon, l'}\rangle$ given by Eq. (2.35).

2.2.3 Bound state wave function

The bound state radial wave function of Eq. (2.27) normalized to unity is given by the following

$$|P_{n,l}\rangle = G_l V |F_l\rangle \frac{1}{N} \quad (2.36)$$

Where N is the normalization constant that is evaluated explicitly in Appendix C. It should be noted that the bound state radial functions are also real.

2.2.4 Functional forms

The bound and continuum wave functions discussed above are general expressions applicable to many possible core potentials. What makes these wave functions desirable in this work is that the $G_l V |F_l\rangle$ terms and all other matrix elements specified can be evaluated analytically when the variational trial function is of the following Slater form

$$|F_l\rangle = r^{l+1} e^{-b_l r} \quad (2.37)$$

(with b_l being the only variational parameter) and the potential V is the screened Coulomb potential given in Eq. (2.16). The necessary matrix elements and some important limiting cases are evaluated explicitly in Appendix C. The evaluated result for $G_l V |F_l\rangle$ is

$$\begin{aligned} G_l V |F_l\rangle = & \lambda (4r)^{l+1} X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2 \sin(\pi\tau)} \right) \\ & \times \int_c dw w^{-\tau+l} (D_l w + 1)^{-2l-2} \exp \left[X \tau \frac{(D_l w - 1)}{(D_l w + 1)} \right] \end{aligned} \quad (2.38)$$

where:

$$\begin{aligned} X &= \kappa = \sqrt{-2E} = \frac{\gamma}{(n - \mu)} \\ \tau &= \frac{\gamma}{X} \end{aligned}$$

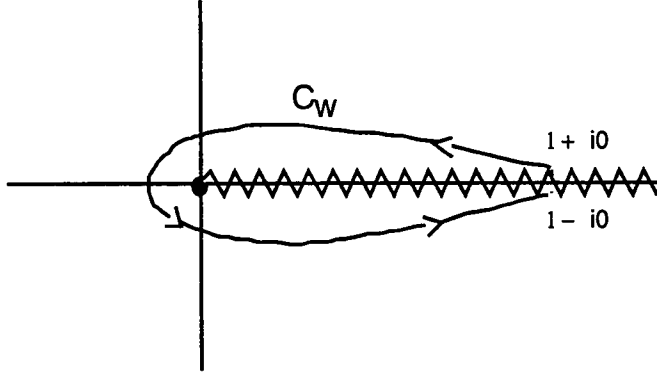


Figure 2-1: The integration contour for $G_l V |F_l\rangle$. Shown are the pole at $w = 0$, the branch cut ($0 \rightarrow +\infty$), and the contour limits of $1 \pm i0$.

$$D_l = \frac{(X - b_l - c)}{(X + b_l + c)}$$

with the contour given in Figure 2-1 [see Appendix A for the mathematical details of derivation]. The above expression with its contour integration is most useful for the bound state where there is a pole at $w = 0$ and a branch cut from $w = 0 \rightarrow +\infty$.

The relevant expression for the continuum function of Eq. (2.35) is derived from Eq. (2.38) by setting $X = -ik$:

$$\begin{aligned} G_{l'}(-X)V|F_{l'}\rangle &= G_{l'}(+ik)V|F_{l'}\rangle \\ &= \lambda(4r)^{l'+1} (+ik)^{2l'+1} (+ik + \tilde{b}_{l'} + c)^{-2l'-2} \left(\frac{ie^{\pi\gamma/k}}{2\sin(\pi\gamma/ik)} \right) \\ &\quad \times \int_c d\rho \rho^{\frac{\gamma}{ik} + l'} (\tilde{\mathcal{D}}_{l'} \rho + 1)^{-2l'-2} \exp \left[+ikr \frac{(\tilde{\mathcal{D}}_{l'} \rho - 1)}{(\tilde{\mathcal{D}}_{l'} \rho + 1)} \right] \end{aligned} \quad (2.39)$$

where:

$$\tilde{\mathcal{D}}_{l'} = \frac{(+ik - \tilde{b}_{l'} - c)}{(+ik + \tilde{b}_{l'} + c)}$$

The continuum state function uses the same contour specified above for the bound state, but there is no pole at $\rho = 0$, though the branch cut remains.

The above wave functions are continuous across the ionization threshold as the functions must be in an appropriate theory [see Appendix B for the mathematical

details]. Further, Maleki[34] showed that for these wave functions the fundamental equation of quantum defect theory Eq. (1.1) is satisfied; *i.e.* $\pi\mu \leftrightarrow \delta$ across the ionization threshold.

2.2.5 Similarity to hydrogen wave functions

As was mentioned in the introduction, the above wave functions are the simplest analytic functions that include the quantum defect in a non-trivial manner. As such these wave functions represent the only complete wave functions for multi-electron atoms that fill the void between the overly simple hydrogenic wave functions and complex numerical wave functions. In fact it is possible to cast the bound state functions of Eq. (2.36) in a form that closely mirrors the hydrogenic functions.

Making the following variable transformations on the integral of Eq. (2.38)

- 1) $t = (Dw - 1)/(Dw + 1)$,
- 2) $\zeta = (t - 1)/2$,
- 3) $h = \zeta/(\zeta - 1)$

yields the following functional dependence

$$G_l V|F_l\rangle \propto r^{l+1} e^{-\frac{\gamma}{(n-\mu)}r} \int_{c_h} dh \frac{\exp\left[\frac{2\frac{\gamma}{(n-\mu)}r h}{1+h}\right] h^{l-(n-\mu)}}{(1+h)^{2l+2}} \quad (2.40)$$

where the contour is given in Figure 2-2. The limit of the h-contour is

$$\Delta = \frac{(b+c-\frac{\gamma}{n-\mu})}{(b+c-3\frac{\gamma}{n-\mu})} \quad (2.41)$$

and the path of integration starts at $\Delta + i0$, circles the origin counter-clockwise, and returns to $\Delta - i0$. This should be compared to the functional dependence of the bound state hydrogen functions[1]

$$\phi_H \propto r^{l+1} e^{-\frac{1}{n}r} {}_1F_1\left[-(n-l-1), 2l+2; 2\frac{1}{n}r\right]$$

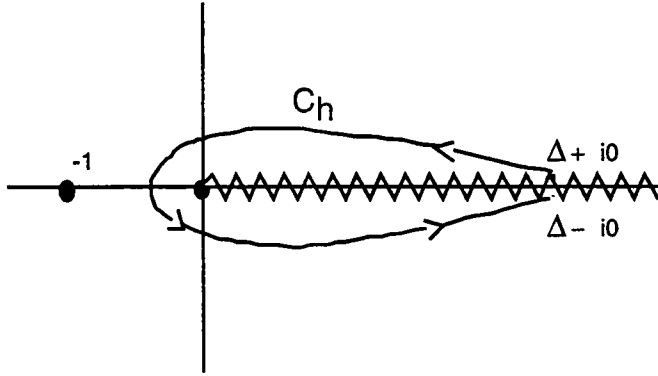


Figure 2-2: The integration contour for the hydrogen-like $G_l V|F_l\rangle$. Shown are the poles at $h = 0, -1$, the branch cut ($0 \rightarrow +\infty$), and the contour limits of $\Delta \pm i0$.

$$\propto r^{l+1} e^{-\frac{1}{n}r} \int_{(0,\infty)} dh \frac{\exp\left[\frac{2\frac{1}{n}r h}{1+h}\right] h^{l-n}}{(1+h)^{2l+2}} \quad (2.42)$$

where the contour is the same as above, but it starts at $+\infty + i0$, circles the origin counter-clockwise and returns to $+\infty - i0$. In the special case of hydrogen bound states there is no branch cut so the contour collapses to a circle around the pole at the origin. Thus one observes that the differences between the bound state Schwinger function and the hydrogen bound state function are the limits of the contour integral and the substitution of $(n - \mu)$ for n . It is because of the difference in contour limit and the branch cut that, even for a high n state, the Schwinger wave function does not become hydrogenic; even though the difference between $n = 50$ and $n - \mu = 49.6$ may seem numerically very small.

It was shown by Maleki[34] that the Schwinger wave function becomes hydrogenic in the limit $\mu \rightarrow 0$. With the similarity of form demonstrated above one can observe by inspection that in the limit $\mu \rightarrow 0$ of Eq. (2.40), the branch cut vanishes and the Schwinger contour collapses to a circle around the origin just as it is in the branchless bound hydrogen case, while the integrand become identical to the hydrogenic case.

The confluent hypergeometric function can also be expressed in the following

power series by expanding the exponential function in a power series

$$\begin{aligned} {}_1F_1(a, b; x) &= \frac{\Gamma(b)}{\eta\Gamma(a)\Gamma(b-a)} \sum_{j=0}^{\infty} \frac{x^j}{j!} \int_{(0,\infty)} dh \frac{h^{a+j-1}}{(1+h)^{b+a}} \\ &= \frac{\Gamma(b)}{\Gamma(a)\Gamma(b-a)} \sum_{j=0}^{\infty} B(a+j, b-a) \frac{x^j}{j!} \end{aligned} \quad (2.43)$$

where $\eta = 1$ if the contour can be reduced to a line integral (*i.e.* NO pole at $h = 0$), or $\eta = e^{2\pi ia} - 1$ if the contour must circle the origin (*i.e.* a pole at $h = 0$). The integral was evaluated to a beta function, $B(a+j, b-a)$, [see Ref. [38], Eq. 8.380(3)]. Performing the same expansion on the integral of Eq. (2.40) yields a similar expression

$$\sum_{j=0}^{\infty} \frac{x^j}{j!} \int_{(c_h)} dh \frac{h^{a+j-1}}{(1+h)^{b+a}} \quad (2.44)$$

which evaluates to [see Ref. [38], Eq. 8.391]

$$\sum_{j=0}^{\infty} B_{\Delta}(a+j, b-a) \frac{x^j}{j!} \quad (2.45)$$

where $B_{\Delta}(a+j, b-a)$ is the incomplete beta function. Thus one could define an “incomplete confluent hypergeometric” ${}_1F_{1\Delta}$ where the complete beta function in Eq. (2.43) is replaced by the incomplete beta function

$${}_1F_{1\Delta}(a, b; x) = \frac{\Gamma(b)}{\Gamma(a)\Gamma(b-a)} \sum_{j=0}^{\infty} B_{\Delta}(a+j, b-a) \frac{x^j}{j!}. \quad (2.46)$$

Now we find that we can re-write Eq. (2.40) as

$$G_l V |F_l\rangle \propto r^{l+1} e^{-\frac{\gamma}{(n-\mu)}r} {}_1F_{1\Delta} \left[-((n-\mu) - l - 1), 2l + 2; 2\frac{\gamma}{(n-\mu)}r \right] \quad (2.47)$$

which should be compared to the hydrogenic case in the first line of Eq. (2.42). For the continuum wave function of Eq. (2.35), one can see directly that if the phase shift δ_l goes to zero, then the coefficient of $GV|F_l\rangle$, which contains $\sin(\delta_l)$, goes to zero. The removal of the $GV|F_l\rangle$ term leaves only the hydrogenic function for the continuum. The above exercise directly shows the connection between the Schwinger

wave functions and the hydrogenic wave functions. It further demonstrates that the Schwinger functions can be thought of as a generalization of the hydrogenic functions for a non-hydrogenic case.

In this simple theory where the variational trial function $|F_l\rangle$ includes only one Slater-type orbital, the range of accessible quantum defects is $0 \leq \mu \leq 1$. However, it was shown by direct computation that $\mu > 1$ is possible if a super-position of Slater orbitals is used as the trial function[34].

2.2.6 Application

To apply the Schwinger wave functions it is necessary to carry out a variational optimization as described in section 2.2.1. In this case, the trial function of Eq. (2.37) has only one variational parameter b_l . It is necessary to specify the core potential V of Eq. (2.16) by a choice of “the range parameter” c , then the minimization can proceed. The variational minimization of $\cot \delta$ at threshold is carried out numerically, and c is adjusted to give good agreement between the variationally optimized δ at threshold and the experimental threshold $\delta = \mu\pi$. In principle the variational parameter b_l could be treated as a function of the state energy. Notwithstanding, b_l is a slowly varying function of energy and it can be variationally optimized for one energy and then used at all energies without significant error. Moreover, fixing b_l for all energies automatically insures that all bound state and continuum state wave functions are orthonormal[34].

In practice, the range parameter c is chosen to give optimized phase shifts δ_l that agree with experimental values at threshold, or with the quantum defect at some high n . This seems to give physically reasonable c values as well as good bound state energy agreement. Threshold was chosen as the reference energy to fix b_l because this work focuses mainly on the near threshold region where a Cooper minimum has a

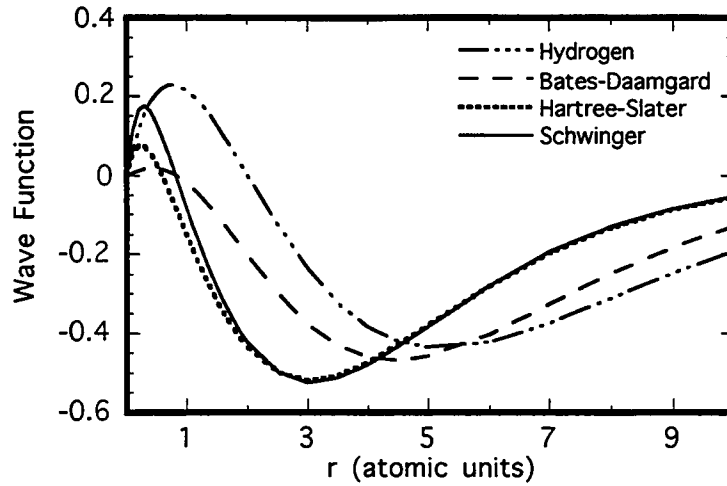


Figure 2-3: The Li(2s) wave function comparison. The Schwinger function is compared to the Li(2s) Hartree-Slater[39] wave function shown with the hydrogen(2s) and Bates-Damgaard[30] Li(2s) wave functions for reference. The Schwinger function has $\mu_S = 0.4115$, the Hartree-Slater function has $\mu_{H-S} = 0.405$, while the experimentally measured quantum defect is $\mu_{2s} = 0.4103$.

large impact on the photo-excitation spectrum. However, fixing b_i does not fix the phase shift/quantum defect for all energy. In fact, the bound state quantum defects show energy variation that closely matches the variation observed experimentally [see Table 2.1, to be discussed later].

Figure 2-3 compares the lithium 2s wave functions of the standard Hartree-Slater theory[39] to the Schwinger wave function $|P_{n,l}\rangle$ of Eq. (2.36). The 2s hydrogen wave function and the Bates-Damgaard[30] lithium 2s wave function are included for reference. It is seen from Figure 2-3 that the wave function of the Bates-Damgaard approximation is very approximate, and not of sufficient quality to be an accurate predictor of Cooper minima. Thus the limited results of the Bates-Damgaard approximation photo-absorption calculations[30] are not referenced further in this work. The range parameter $c = 1.7$ for this calculation was chosen to best fit the experimentally measured threshold quantum defect. The wave functions generated by the variational

method described above are a significant improvement over the hydrogenic functions, and the semi-empirical Bates-Daamgaard. Furthermore, the variational Schwinger wave function roughly approaches the numerical wave function. It is clearly seen that at large radius $r > 5$, the Schwinger and Hartree-Slater wave functions are indistinguishable. While for $r < 1$ the two wave functions diverge. This level of agreement is impressive from such a simple theory, particularly since a ground state is hardly the type of Rydberg state this Schwinger theory was intended to treat. Few would argue that the simple screened potential of Eq. (2.16), and the absence of electron exchange, could give a complete picture for a ground state wave function. It is also interesting to note that, the experimentally measured[40] quantum defect for the lithium 2s state is 0.4115, while the Hartree-Slater and Schwinger wave functions have quantum defects of 0.405 and 0.4103 respectively.

Shown in Figure 2-4(a) are the wave functions generated for the Rydberg series of Li(ns) for $n = 2 - 5$ which shows the typical progression of nodes and final anti-nodes familiar from the hydrogenic functions. Figure 2-4(b) shows the high n progression of the same Rydberg series for $n = 10, 20, 50$ and one near threshold continuum state (with energy $\varepsilon = +0.02\text{eV}$), with all wave functions normalized to unit energy to readily show the similarities. The stabilization of the wave function nodes for high n and the smooth transition across threshold into the continuum states is clearly evident. Figure 2-3 showed that the Schwinger wave functions are quite good at large radius, and since the amplitude of the higher Rydberg states is mainly at large radius, one would expect good agreement with complicated numerical wave functions for high n .

The quantum defects of the lithium $l = 0$ and $l = 1$ Rydberg series are given in Table 2.1, which also shows the experimental values[40, 41]. As can be seen, the trend of the calculated quantum defects is similar to the experimental values and a similar

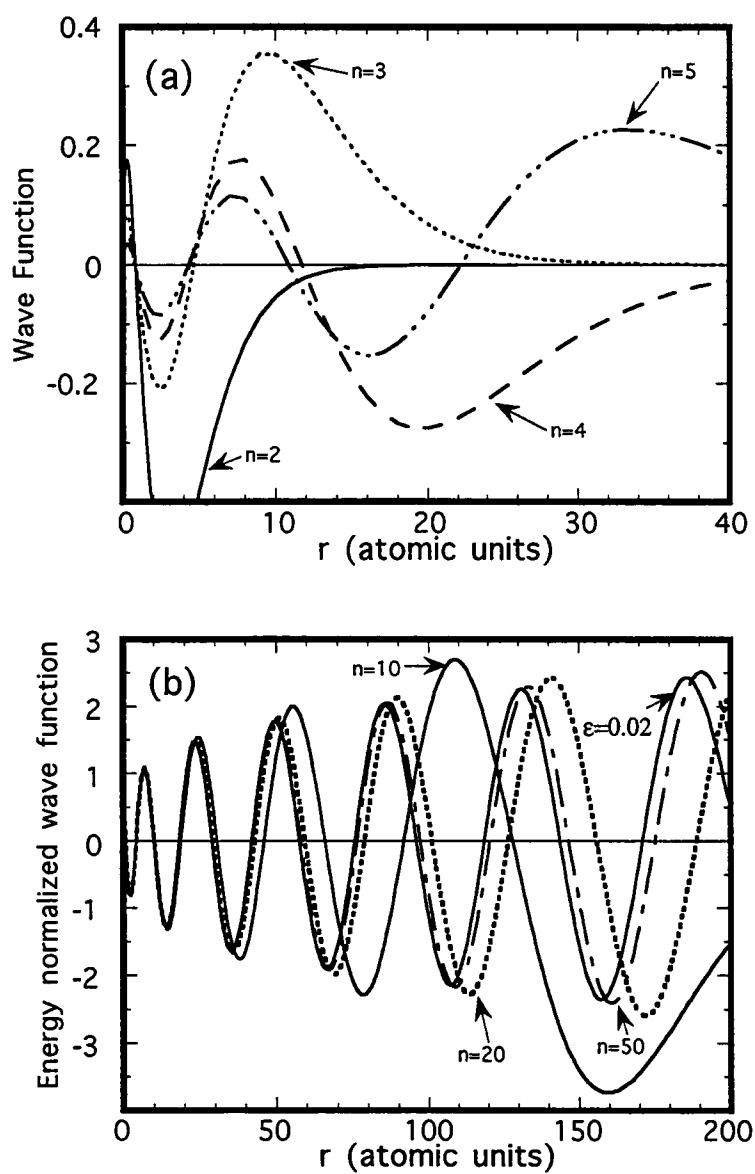


Figure 2-4: The Schwinger wave functions of the Li(ns) Rydberg series. Shown are, (a) the $n = 2 - 5$ wave functions normalized to unity; (b) the $n = 10, 20, 50$ wave functions and the near threshold continuum state $\epsilon=0.02\text{eV}$ all normalized to unit energy.

Table 2.1: Quantum defects for Li, $l = 0, 1$ Rydberg series of states calculated by this work compared to experimental values[39, 40]. Each series is organized by principle quantum number n .

n	$l = 0$		$l = 1$	
	this work	experiment	this work	experiment
2	0.4103	0.4115	0.0392	0.0407
3	0.4039	0.4039	0.0440	0.0444
4	0.4020	0.4018	0.0455	0.0457
5	0.4015	0.4009	0.0462	0.0462
6	0.4009	0.4004	0.0465	0.0465
7	0.4006	0.4002	0.0467	0.0467
8	0.4005	0.4000	$\vdots$	
$\vdots$	$\vdots$			
∞	0.40002		0.0473	

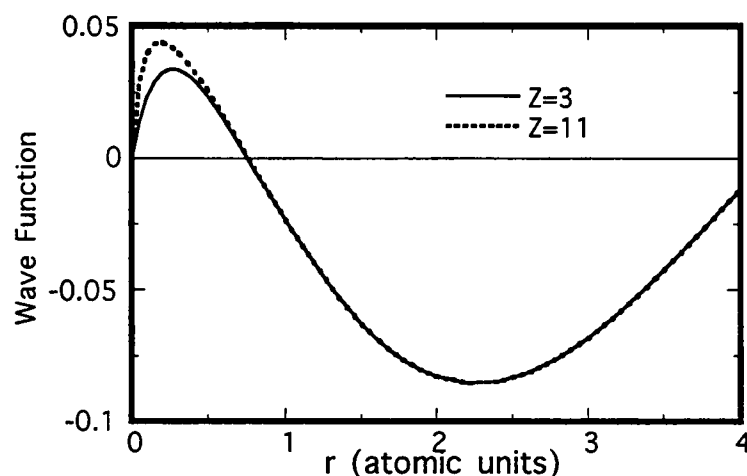


Figure 2-5: A comparison of two $n = 5$ wave functions with the same quantum defect $\mu = 0.42$ but different nuclear charges $Z = 3$ and $Z = 11$.

level of agreement with experiment is observed in both the lithium $l = 0$ and $l = 1$ Rydberg series. The range parameters used in these calculations are $c_0 = 1.7$ and $c_1 = 2.36$ for the $l = 0$ and $l = 1$ series respectively. This difference in c amounts to difference in the corresponding core radius of $r_{c_0} = 0.59$ and $r_{c_1} = 0.42$. These different core radii are reasonable, considering that the $l = 0$ wave functions penetrate the core region more than the $l = 1$ wave functions. The greater core penetration of the $l = 0$ states should lead to a more diffuse (*i.e.* larger) core than the $l = 1$ core. In effect, the penetration of the core by the $l = 0$ state provides some screening for the electrons of the core, so the core expands slightly.

In this Schwinger approximation the wave function is only slightly dependent on the nuclear charge Z *via* the core strength parameter $\lambda = -(Z - 1)$. Shown in Figure 2-5 is a comparison of two 5s wave functions with the same quantum defect $\mu = 0.42$. One wave function is for $Z = 3$, while the other wave function is for $Z = 11$. Asymptotically, the wave functions are indistinguishable on the scale of the graph.

But, at small radius the wave functions are different with the higher Z function having the larger amplitude. To achieve identical quantum defects of $\mu = 0.42$ required vastly different range parameters c for the two wave functions. The $Z = 3$ function required $c = 1.338428$, while the $Z = 11$ function required $c = 14.9904$. These core range parameters equate to approximate core radii of $r_c = 0.749$ and 0.0667 for the $Z = 3$ and 11 functions respectively.

2.3 Radial Dipole Matrix

With the radial wave functions given in the previous section one can now evaluate the radial dipole matrix element R for bound-bound and bound-continuum transitions.

For bound-bound transitions one uses Eq. (2.36) for both wave functions. The initial wave function P_{nl} uses the un-primed quantities while the final wave function $P_{n'l'}$ uses the prime and tilde quantities. The details of the evaluation of $R_{n'l';nl}$ are given in the Appendix D, only the result is given here.

$$\begin{aligned}
R_{n'l';nl} &= \langle P_{n'l'} | r | P_{nl} \rangle \\
&= \frac{1}{N_{n'l'} N_{nl}} (-\lambda^2) 4^{l'+l+2} (l' + l + 3)! X^{2l+1} (X + b_l + c)^{-2l-2} \\
&\quad \times (\tilde{X})^{2l'+1} (\tilde{X} + \tilde{b}_{l'} + c)^{-2l'-2} \left(\frac{ie^{i\pi\tilde{\tau}}}{2 \sin(\pi\tilde{\tau})} \right) \\
&\quad \times \sum_{j=0}^{l'-l+2} \binom{l' - l + 2}{j} \frac{D_l^j}{(-\tau + l + j + 1)} \int_c d\rho \rho^{-\tilde{\tau}+l'} \frac{(1 + \tilde{D}_{l'} \rho)^{l-l'+2}}{[N(\rho)]^{l'+l+4}} \\
&\quad \times {}_2F_1 \left(-\tau + l + j + 1, l + l' + 4; -\tau + l + j + 2; \frac{M(\rho)}{N(\rho)} \right) \quad (2.48)
\end{aligned}$$

where:

$$M(\rho) = D_l [E_- + \tilde{D}_{l'} E_+ \rho]$$

$$N(\rho) = E_+ + \tilde{D}_{l'} E_- \rho$$

$$\begin{aligned}
E_+ &= X + \tilde{X} \\
E_- &= X - \tilde{X} \\
\tilde{X} &= \frac{\gamma}{(n' + \mu')} \\
\tilde{\tau} &= \frac{\gamma}{\tilde{X}}
\end{aligned}$$

For a bound-continuum transition, Eq. (2.36) represents the initial bound state P_{nl} while Eq. (2.35) represents the final continuum state $P_{El'}$. Thus the radial dipole matrix element is given by

$$\begin{aligned}
R_{El',nl} &= \langle P_{\epsilon,l'} | r | P_{n,l} \rangle \\
&= \frac{1}{\sqrt{\pi}N} \left(e^{i\delta_{l'}} \langle f_{l'} | r \{ G_l V | F_l \} \rangle \right. \\
&\quad \left. + \frac{\sin(\delta_{l'})}{\langle f_{l'} | V | F_{l'} \rangle} \{ \langle F_{l'} | V G_{l'}^* (+ik) \rangle r \{ G_l V | F_l \} \} \right) \\
&= \frac{1}{\sqrt{\pi}N} \left(e^{i\delta_{l'}} R^c + \frac{\sin(\delta_{l'})}{\langle f_{l'} | V | F_{l'} \rangle} R^s \right) \tag{2.49}
\end{aligned}$$

The dipole matrix separates into two terms because of the two terms of the continuum wave function; R^c is that part with the Coulombic final state $\langle f_{l'} |$ term, R^s is the part that has the screened atomic core perturbation in the final state $\langle F_{l'} | V G_{l'}^* (+ik)$ term. The mathematical details of the evaluation of R^c and R^s are given in Appendix D, the results are listed here:

$$\begin{aligned}
R^c &= \lambda \frac{2^{2l+l'+2+\frac{1}{2}}}{\Gamma(2l'+2)} \Gamma(l+l'+4) X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\
&\quad \times k^{l'+\frac{1}{2}} \exp\left(\frac{\pi\gamma}{2k}\right) |\Gamma(l'+1 + i\frac{\gamma}{k})| \\
&\quad \times \int_c dw w^{-\tau+l} (D_l w + 1)^{-2l-2} \left[-X \frac{(D_l w - 1)}{(D_l w + 1)} - ik \right]^{-l-l'-4} \\
&\quad \times {}_2F_1 \left(l'+1 - i\frac{\gamma}{k}, l+l'+4; 2l'+2; \frac{2ik}{\left[X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \right]} \right) \tag{2.50}
\end{aligned}$$

$$\begin{aligned}
R^s = & (-1)^{-l-l'-3} \lambda^2 4^{l'+l+2} (l'+l+3)! X^{2l+1} (X + b_l + c)^{-2l-2} \\
& \times (-ik)^{2l'+1} (-ik + \tilde{b}_{l'} + c)^{-2l'-2} \left(\frac{ie^{i\pi\tau}}{2 \sin(\pi\tau)} \right) \\
& \times \sum_{j=0}^{l-l'+2} \binom{l-l'+2}{j} \frac{(\tilde{\mathcal{D}}_{l'}^*)^j}{(\frac{\gamma}{ik} + l' + j + 1)} \int_c dw w^{-\tau+l} \frac{(D_l w + 1)^{-2l-2}}{[\mathcal{N}(w)]^{l+l'+4}} \\
& \times {}_2F_1 \left(\frac{\gamma}{ik} + l' + j + 1, l + l' + 4; \frac{\gamma}{ik} + l' + j + 2; -\frac{\mathcal{M}(w)}{\mathcal{N}(w)} \right) \quad (2.51)
\end{aligned}$$

where:

$$\mathcal{M}(w) = \tilde{\mathcal{D}}_{l'}^* [D_l \mathcal{E}_- w - \mathcal{E}_+]$$

$$\mathcal{N}(w) = D_l \mathcal{E}_+ w - \mathcal{E}_-$$

$$\mathcal{E}_+ = X + ik$$

$$\mathcal{E}_- = X - ik$$

It was noted earlier in section 2.2 that the wave functions are real, which means the radial dipole matrix R will be real for both bound-bound and bound-continuum wave functions.

The radial dipole matrices given by Eqs. (2.48), and (2.49) may appear difficult to evaluate because of the one remaining complex contour integration. Notwithstanding, the remaining contour integral is easily programmed and evaluated with MathematicaTM [42]. The only difficulty is the unusual branch-cut $(0, +\infty)$, which requires splitting the complex plane along the real axis and forcing the proper phase for the $w^{-\tau}$ terms. The program was run efficiently on an Apple MacintoshTM 7100/66. The choice of MathematicaTM as the programming language and a Macintosh as the computational platform makes the very limited computational aspects of this theory highly accessible.

As was shown in Chapter 2 section 2.2.5, the hydrogen wave functions are the

$\mu = 0$ and $\delta = 0$ limits of the Schwinger wave functions. Thus a useful limit of the radial dipole matrix element R is when one wave function is hydrogenic. These limit forms of R are useful in determining trends in the location of Cooper minima that depend only on the difference of quantum defects $\Delta\mu = \mu_f - \mu_i$ of the initial and final state wave functions. The derivation of these forms is nearly identical to that for two Schwinger states.

Section 2.1 stated that a Cooper minimum occurs in the photo-excitation spectrum when the radial dipole matrix element changes sign and passes through zero. Such a Cooper minimum is shown in Figure 2-6. The calculations shown display the radial dipole matrix and cross section for the $n = 5, l_i = 0 \rightarrow E, l_f = 1$ transitions in a hypothetical atom with $Z = 11$, $\mu_i = 0.785$, and $\mu_f = 0.361$. These plots show a Cooper minimum in the cross section plot at $E \approx 0.1 \text{ eV}$ and the zero of the radial dipole matrix element at the same energy. The hydrogen radial dipole matrix elements R_H are positive definite and monotonically decreasing in contrast to R_{l+1} shown in Figure 2-6(a). At energies below the Cooper minimum, R_{l+1} is negative. At energies above the Cooper minimum R_{l+1} is positive. The fact that there is a Cooper minimum in this calculation proves that a quantum defect difference is sufficient to produce a minimum without the need for more complex phenomena like electron exchange or core polarization.

To compare the dipole matrix elements of this theory with experimental results, it is convenient to plot the oscillator strength density of this work with experimentally measured values. This comparison is shown in Figure 2-7 for the lithium atom transitions from $n = 2, l_i = 0$ to $E, l_f = 1$. The experimental values are from Ref. [6], and [7]. The calculations used the Schwinger Li(2s) wave function (with $c = 1.7$) shown in Fig. 2-3, and the Li p-state wave functions (with $c = 2.36$) for the quantum defects given in Table 2.1. The level of agreement between this theory and the experimental

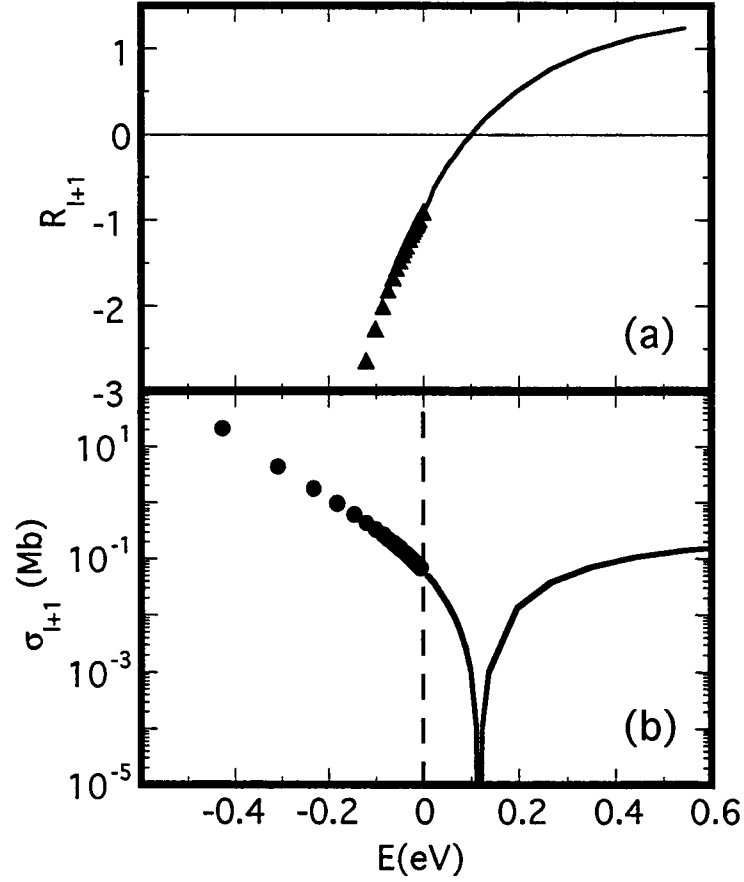


Figure 2-6: The relationship between Cooper minima in the cross section and the zero of the radial dipole matrix element. (a) the radial dipole matrix element R_{l+1} showing a zero at $E \approx 0.1 \text{ eV}$; (b) the cross section σ_{l+1} showing a Cooper minimum at $E \approx 0.1 \text{ eV}$. These plots are for $n = 5$ $l_i = 0 \rightarrow E, l_f = 1$ with $Z = 11$, $\mu_i = 0.785$, and $\mu_f = 0.361$.

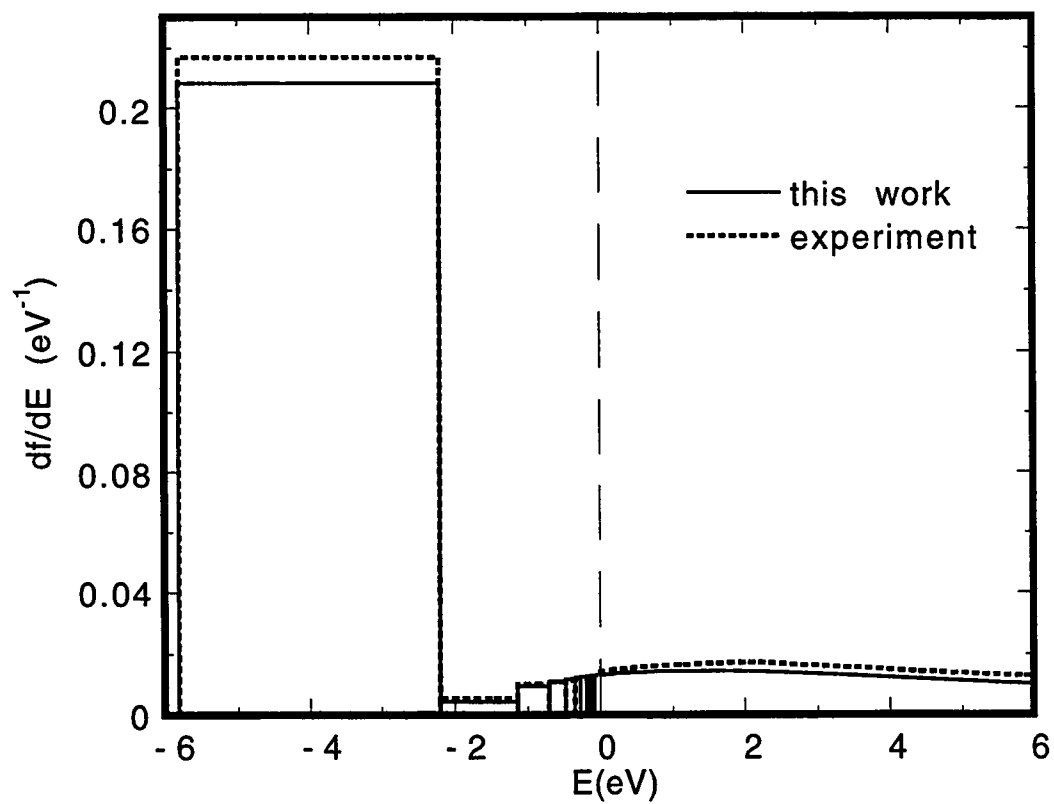


Figure 2-7: The oscillator strength spectrum for the bound-bound and bound-continuum transitions of the Li(2s) state. Shown here is this work and experiment[6,7].

values is quite high especially for a ground state considering the approximate nature of this theory. The main disagreement is in the $2s \rightarrow 2p$ transition and the $2s \rightarrow \epsilon p$ transitions into the continuum. Other more sophisticated calculations by Lahiri and Manson[22] using Hartree-Slater codes and Amusia *et.al.*[43] using random-phase approximation also calculate values that are about 30% below experiment[7]. This has lead to the suggestion[22] that the experimental measurements[7] of the lithium $2s \rightarrow \epsilon p$ cross sections could contain some contamination from Li_2 photoionization and this might lead to unrealistically large cross sections. So the lack of agreement in the bound-continuum range of Fig. 2-7 could be due to inaccuracies in the experiment.

The Schwinger theory shows the Cooper minimum to be somewhere between the $2p$ and $3p$ state, but because of the discrete nature of the bound states, the exact location and shape of the Cooper minimum cannot be determined. Examination of the radial dipole matrix elements as a function of energy (not shown) reveals a change in sign from negative for $2s \rightarrow 2p$ to positive for $2s \rightarrow 3p$ and higher p -states, just as was demonstrated in Figure 2-6.

It is also interesting to test the sum rule of Eq. (2.11). The sum of all bound state oscillator strengths and the corresponding integral over continuum state oscillator strength densities should be unity. This would be the total area under the solid line curve of Fig. 2-7 if the graph were extended to infinite positive energy. For this Schwinger theory as applied above to the $\text{Li}(2s)$ state, the sum rule of Eq. (2.11) gives 0.9986, which is surprisingly close to 1, as it would be in a completely accurate theory.

Chapter 3

Results and Discussion

3.1 General Studies of Cooper Minima

3.1.1 Movement of Cooper minima with changes in $\Delta\mu$

It has been mentioned in the literature many times that the location of Cooper minima is dependent on the difference in quantum defect $\Delta\mu = \mu_f - \mu_i$ of the final and initial state wave functions. With this theory, where the quantum defect enters directly as a parameter, it is easy to study the location dependence of the Cooper minimum with respect to $\Delta\mu$. In this study the notation E_{CM} will be used to denote “the energy at which a Cooper minimum occurs” in the photo-excitation spectrum. This study will also express energies in Rydbergs: $1 \text{ Rydberg} = 1\text{Ry} = 13.6\text{eV} = 1/2$ “an atomic unit of energy”. Rydbergs seem to be the most appropriate units for discussing the results of this Cooper minimum project since the energy of the hydrogen 1s ground state is 1Ry.

Since the hydrogen wave function is a limiting case of the Schwinger wave functions, it is reasonable to use a hydrogen wave function for one of the states in the

radial dipole matrix element so that one state's quantum defect is fixed at $\mu = 0$. For the $l \rightarrow l + 1$ transitions it is convenient to use a hydrogenic state for the final wave function; thus $\mu_f = 0$ and $\Delta\mu = -\mu_i$. Figure 3-1 gives a preliminary look at the trajectory of the Cooper minimum when $\Delta\mu$ changes. These calculations show the photo-excitation cross section for the $n_i = 5, l_i = 1 \rightarrow E, l_f = 2$ transition of hypothetical atoms with nuclear charge $Z = 11$, plotted as a function of final state energy. The quantum defect of the initial state is varied from $\mu = 0.00042$ to 0.5858 , thus the $\Delta\mu$ changes from -0.00042 to -0.5858 . The change of $\Delta\mu$ causes the Cooper minimum to migrate in energy from below the $n_f = 6, l_f = 2$ ($\Delta\mu = -0.00042$) state, up through the bound states and into the continuum states $E, l_f = 2$ ($\Delta\mu = -0.5858$). Figure 3-2 shows the continuation of this trend for $\Delta\mu = -0.8263$ to $\Delta\mu = -0.96287$. It is observed that as $\Delta\mu \rightarrow -1$ the Cooper minimum moves rapidly toward higher energy.

This trend, of a Cooper minimum appearing in the bound states for small $\Delta\mu$ and moving up through the bound states into the continuum as $\Delta\mu$ becomes more negative, holds true for all $l \rightarrow l + 1$ transitions. Figure 3-3 shows the locations of the Cooper minima E_{CM} as a function of $\Delta\mu$ for $l \rightarrow l + 1$ transitions from an initial $n = 5$ Schwinger bound state to a final hydrogen state. Shown in the Figure 3-3 are the transitions, $l = 0 \rightarrow 1$, $l = 1 \rightarrow 2$, and $l = 2 \rightarrow 3$. The movement of the Cooper minimum is most dramatic for the $l = 0 \rightarrow 1$ transitions where the Cooper minimum appears at threshold for $\Delta\mu \approx -0.35$ and then moves gradually higher in energy as $\Delta\mu$ decreases toward -1 . For the higher l transitions the movement of the Cooper minimum above threshold occurs for progressively more negative $\Delta\mu$, and the rapid movement toward higher energy is compressed into a smaller range of $\Delta\mu$.

For $l \rightarrow l - 1$ transitions it is convenient to use a hydrogenic function for the initial state and a Schwinger function for the final state; thus $\mu_i = 0$ and $\Delta\mu = \mu_f$. It is

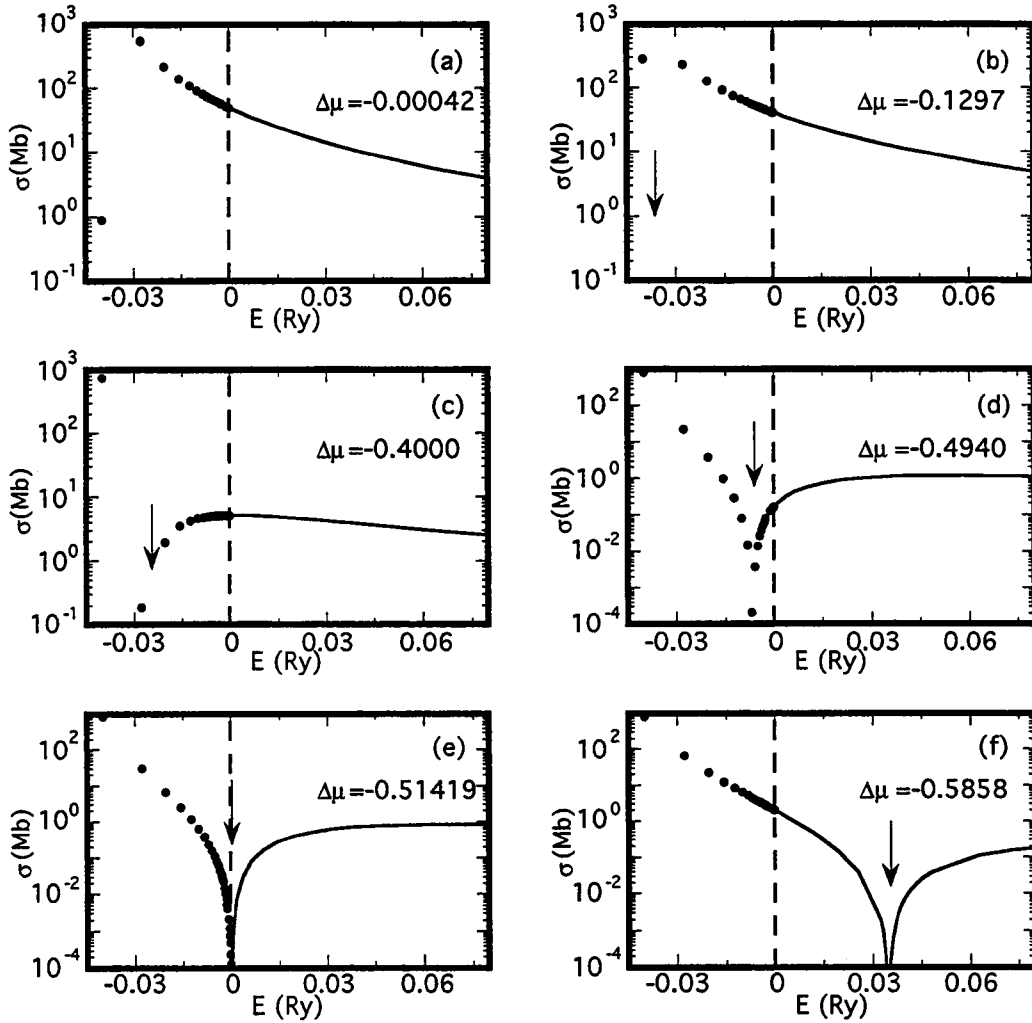


Figure 3-1: The migration of the Cooper minimum with changes in $\Delta\mu$ for $l \rightarrow l+1$ transitions. Shown are the cross sections for the $n_i = 5, l_i = 1 \rightarrow E, l_f = 2$ transition of hypothetical atoms with nuclear charge $Z = 11$ in the range $-0.00042 < \Delta\mu < -0.5858$. the horizontal axis is the energy of the final state. In these cross section spectra the initial state is a Schwinger function with quantum defect μ_i while the final state is Coulombic ($\mu_f = 0$). For all graphs the $\Delta\mu = -\mu_i$ is given on the graph, and the approximate location of the Cooper minimum is indicated by the arrow.

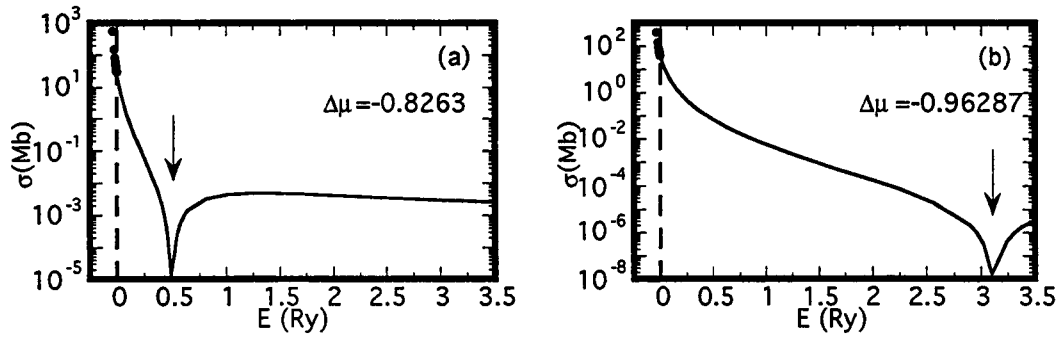


Figure 3-2: A continuation of the migration of the Cooper minimum with changes in $\Delta\mu$ for $l \rightarrow l + 1$ transitions. Shown are the cross sections for the $n_i = 5, l_i = 1 \rightarrow E, l_f = 2$ transition of hypothetical atoms with nuclear charge $Z = 11$ with $\Delta\mu = 0.8263$ and 0.96284 . In these cross section spectra the initial state is a Schwinger function with quantum defect μ_i , while the final state is Coulombic ($\mu_f = 0$). For all graphs the $\Delta\mu = -\mu_i$ is given on the graph, and the approximate location of the Cooper minimum is indicated by the arrow.

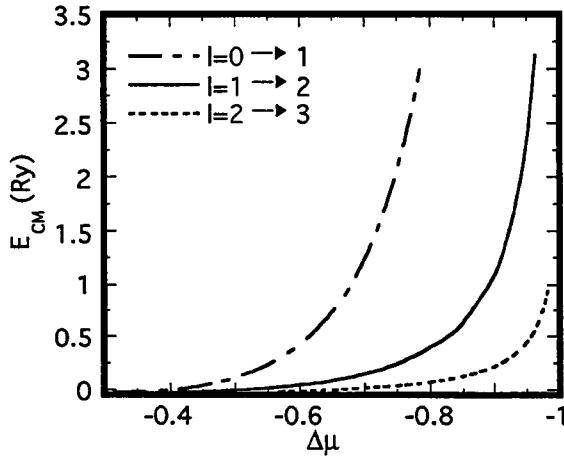


Figure 3-3: The energy E_{CM} of the Cooper minimum as a function of $\Delta\mu = \mu_f - \mu_i$ for $l \rightarrow l + 1$ transitions. All transitions are from an initial $n = 5$ state. Shown are the $l = 0 \rightarrow 1, l = 1 \rightarrow 2, l = 2 \rightarrow 3$ transitions.

also desirable in this model study to fix the final continuum state's $\mu_f = \delta_f/\pi$ at its threshold value for all energies. Normally δ_f varies with energy, and this case will be examined later. Nevertheless, to simplify this initial analysis δ_f is fixed at its threshold value for all energy. Calculations for $l \rightarrow l - 1$ transitions reveal that the location of the Cooper minimum has a very different dependence on $\Delta\mu$, as $\Delta\mu$ deviates more from the hydrogenic $\Delta\mu = 0$. Rather than appearing just above the the first transition energy ($n, l \rightarrow n + 1, l'$) and migrating toward higher energy, the Cooper minima for the $l \rightarrow l - 1$ transitions seem to appear at some higher energy as a pair. One Cooper minimum moves down in energy with increasingly negative $\Delta\mu$. The other Cooper minimum moves up in energy with increasingly negative $\Delta\mu$. Shown in Figure 3-4 is a series of cross section spectra for the $n = 5, l = 1 \rightarrow E, l' = 0$ transitions of hypothetical atoms for which $Z = 11$ and the initial $l = 1$ state is hydrogenic, while the final $l' = 0$ state is a Schwinger function. For this series of $n = 5, l = 1 \rightarrow E, l' = 0$ transitions, it is seen that for $\Delta\mu < 0.64$ there is no Cooper minimum; however, for $\Delta\mu \approx 0.749$ there are clearly two Cooper minima. The Cooper minima start near threshold in the region where the integrand in the radial dipole matrix is highly oscillatory and thus difficult to evaluate of this. The extrapolated point of bifurcation of the Cooper minima is $E \approx 0$ (threshold or very near it) for $\Delta\mu \approx 0.748$. The lower energy Cooper minimum moves below the $n = 7$ final state at $\Delta\mu \approx 0.777$, so the range of this double Cooper minimum effect is very small, and would be very difficult to detect experimentally since it would require a naturally occurring atomic system within the proper range of quantum defects. The only other indication of this Cooper minimum bifurcation in the literature is in a Chinese language paper[32] that predicts paired Cooper minima for $0.6 < \Delta\mu < 1.0$.

Figure 3-5 shows the location of the Cooper minima as a function of $\Delta\mu$ for the $n = 5, l = 1 \rightarrow E, l' = 0$ sequence and the $n = 5, l = 2 \rightarrow E, l' = 1$ sequence

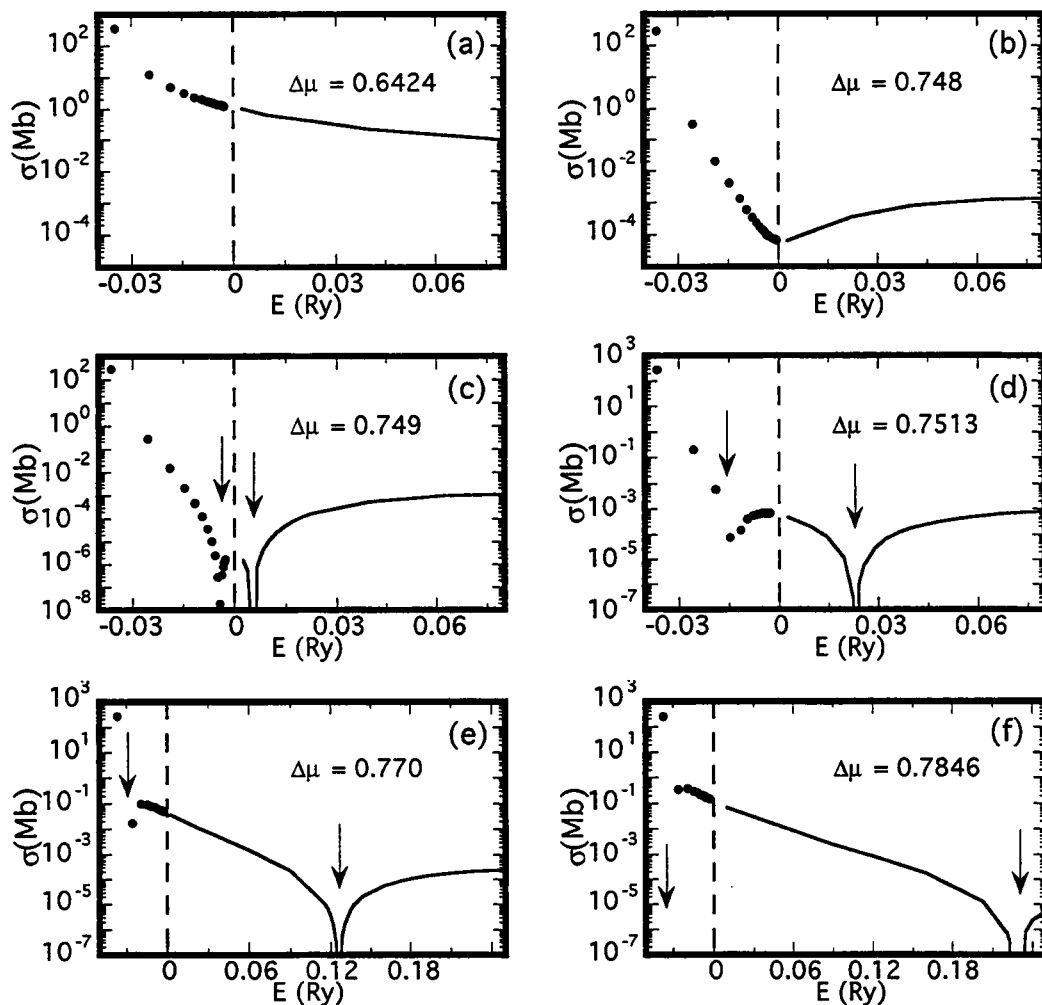


Figure 3-4: The cross sections of $n = 5, l = 1 \rightarrow E, l' = 0$ showing the migration of the Cooper minima for different $\Delta\mu$. Shown are calculations for hypothetical atoms for which $Z = 11$ and the initial $l = 1$ state is hydrogenic, while the final $l' = 0$ state is a Schwinger function. These spectra show the migration of the double Cooper minima with increasingly negative $\Delta\mu$. The $\Delta\mu$ is indicated on each graph, and arrows indicate the approximate locations of the Cooper minima.

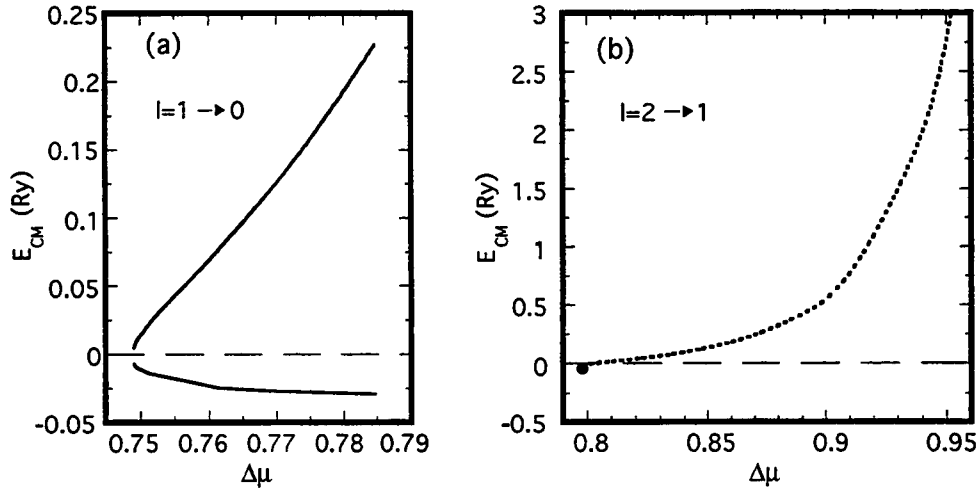


Figure 3-5: The energy E_{CM} of Cooper minimum as a function of $\Delta\mu$ for $l \rightarrow l - 1$ transitions. Shown are calculations of E_{CM} for the $n = 5, l \rightarrow E, l' = l - 1$ for hypothetical $Z = 11$ atoms where the initial l -state is hydrogenic while the final l' -state is a Schwinger function. (a) the trajectory of the double Cooper minima of $l = 1 \rightarrow 0$ transitions. (b) the trajectory of the Cooper minimum of $l = 2 \rightarrow 1$ transitions. The single circle point at $\Delta\mu \approx 0.8$ is the approximate location of the bound state Cooper minimum. The higher energy Cooper minimum trajectory starts approximately 0.0197Ry higher than the circle point in energy in the bound states and crosses the $E = 0$ threshold. Note: the energies of the bound state Cooper minima ($E < 0$) are interpolated points, based on the values of the radial dipole matrix at the bound state energies, and as such are less accurate.

for hypothetical $Z = 11$ atoms where the initial l -state is hydrogenic while the final l' -state is a Schwinger function. The $l = 2 \rightarrow 1$ transitions show only one Cooper minimum, except for $\Delta\mu \approx 0.79795$, where the minima occur between the energies of the $n_f = 6$ and 7 final states and the $n_f = 13$ and 14 final states. The Cooper minimum between $n_f = 13$ and 14 moves across the $E = 0$ threshold toward higher energy with increasing $\Delta\mu$, while the lower energy Cooper minimum moves down farther in the bound states with increasing $\Delta\mu$. For the $l = 2 \rightarrow 1$ transitions, the range in $\Delta\mu$ over which the Cooper minima move is very compressed (as it was for the higher l -state transitions for the $l \rightarrow l + 1$ survey). Because of this extremely small range in $\Delta\mu$ that gives double Cooper minima for $l = 2 \rightarrow 1$ transitions, there is only this one $\Delta\mu$ on the graph showing multiple minima. This one point seems to indicate that the bifurcation of Cooper minima that seems to occur at threshold for the $n = 5, l = 1 \rightarrow E, l' = 0$ sequence with $\Delta\mu \approx 0.748$, is only a coincidence, and threshold is not a privileged location for Cooper minima bifurcation to occur.

Multiple Cooper minima in $l \rightarrow l+1$ transitions have been predicted theoretically[31] for nuclear charges in the range $37 \leq Z \leq 55$, and $\Delta\mu < -2$. It seems unlikely that the multiple minima predicted in Ref.[31] for the $l \rightarrow l + 1$ transitions are related to the apparent bifurcation of minima predicted in the present study because the present study predicts multiple minima for the $l \rightarrow l - 1$ transitions in the $0.748 < \Delta\mu < 0.78$ range.

3.1.2 Explicit dependence on μ

Thus far the dependence of the Cooper minimum energy E_{CM} has been shown to be strongly linked to the quantum defect difference $\Delta\mu$ of the initial and final states. It is also important to consider the dependence of Cooper minimum energy on the actual μ_i and μ_f explicitly. Shown in Figure 3-6 are the cross sections of two hypothetical

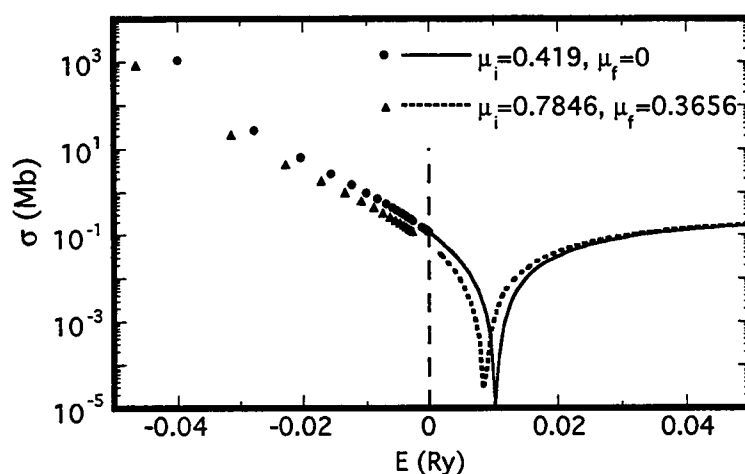


Figure 3-6: Direct dependence of the Cooper minimum on μ_i and μ_f . The cross sections of $n = 5, l = 0 \rightarrow E, l' = 1$ transitions of two hypothetical atoms for which $Z = 11$ and $\Delta\mu = 0.419$. The circle points and solid line show the cross section for $\mu_i = 0.419$ and fixed $\mu_f = 0$ with a Cooper minimum at $E = 0.0104\text{Ry}$. The triangle points and dash line show the cross section for $\mu_i = 0.7846$ and fixed $\mu_f = 0.3656$ with a Cooper minimum at $E = 0.00856\text{Ry}$. The small difference in Cooper minimum energy indicates that the actual values of the quantum defects are far less important than $\Delta\mu$.

atoms with $Z = 11$ for the $n = 5, l = 0 \rightarrow E, l' = 1$, both with $\Delta\mu = 0.419$ but with very different μ_i and μ_f . The circle points and solid line show the cross section for $\mu_i = 0.419$ and fixed $\mu_f = 0$ with a Cooper minimum at $E = 0.0104$ Ry. The triangle points and dash line show the cross section for $\mu_i = 0.7846$ and fixed $\mu_f = 0.3656$ with a Cooper minimum at $E = 0.00856$ Ry. This small energy difference which amounts to 0.025 eV shows that the major determiner of E_{CM} is $\Delta\mu$, while the actual values of the individual quantum defects yield a minor correction to this Cooper minimum energy.

3.1.3 Dependence on nuclear charge Z

If two wave functions have the same quantum numbers and quantum defects but different nuclear charge, the difference in the radial wave functions is small and occurs at a small radius. The difference of two such wave functions was shown in Figure 2-5 for $Z = 3$ and 11. Since the major contribution to the radial dipole matrix element comes from the large radius region of the radial integral (at least for lower Z atoms), one would expect there to be little difference in the photo-excitation cross sections calculated for the two wave functions shown in Figure 2-5. Actual cross section calculations (not shown), that use the initial wave functions shown in Figure 2-5 and hydrogenic final states, show the cross sections are indistinguishable. This result confirms that small differences in the wave functions at small radius have little if any effect on cross sections.

Other studies[10, 31] have examined E_{CM} for many nuclear charges and concluded that there is much structure to the location of Cooper minima as Z is varied; however, this structure is due more to the changes of quantum defect for valence electrons than to the nuclear charge directly.

3.1.4 Dependence on variable δ

In the cross section calculations shown above, the final state phase shift $\delta_f = \pi\mu_f$ was fixed at a constant value such that the phase shift at all energies in the continuum equals the threshold phase shift. This model is excellent for examining the location dependence of Cooper minima on $\Delta\mu$, yet, it is not a good model for examining real atoms. In real atoms the phase shift can vary considerably from its threshold value as the energy of the continuum state increases. For the Schwinger wave functions, energy dependence of δ is a natural consequence within the theory. This energy dependence of δ can be overridden as it was in figures shown above. If the natural energy dependence of the phase shift $\delta_f = \pi\mu_f$ is allowed to occur, the trajectory of E_{CM} can be altered significantly, especially when μ_f starts at a high threshold value. Figure 3-7 shows how the variation of δ_f apparently modifies the trajectory of Cooper minima shown in Figure 3-5(b).

If the variation of δ_f with final state energy E is included in the $\Delta\mu$, $\Delta\mu$ becomes a function of energy $\Delta\mu(E)$. Further, if the above graphical relationships between $\Delta\mu$ and E_{CM} are inverted, we will have functions $\Delta\mu(E_{CM})$ predicting the quantum defect difference based on the energy of the Cooper minimum. When plotted on the same graph, the two curves given by $\Delta\mu(E)$ and $\Delta\mu(E_{CM})$ could intersect. At such an intersection a Cooper minimum is expected. Figure 3-8 shows such an intersection of $\Delta\mu(E)$, for the $n = 5, l = 2 \rightarrow E, l' = 1, \mu_f(\text{threshold}) = 0.944$, and the $\Delta\mu_f(E_{CM})$ curve, for $l = 2 \rightarrow 1$ transitions. [Note: $\Delta\mu_f(E_{CM})$ is the curve in Figure 3-5(b) flipped and rotated.] To simplify the model without loss of generality, the initial state is hydrogenic and the final state is a Schwinger function, thus $\Delta\mu(E) = \delta_f(E)/\pi$. The intersection occurs at $E = 0.72\text{Ry}$ and $\Delta\mu = 0.901$, which corresponds to the energy of the Cooper minimum predicted by the solid line of Figure 3-7. This indicates that the curves of Figures 3-3 and 3-5 are good predictors of the location of Cooper

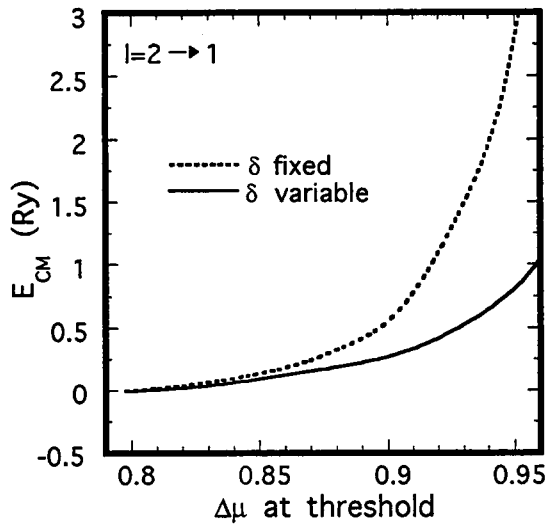


Figure 3-7: The energy E_{CM} of the Cooper minimum as a function of threshold $\Delta\mu$. Shown are the E_{CM} for the $n = 5, l = 2 \rightarrow E, l' = 1$ transitions of hypothetical $Z = 11$ atoms, where the initial l -state is hydrogenic while the final l' -state is a Schwinger function. The dash line is the trajectory of the Cooper minimum when the phase shift δ_f is fixed at the threshold value for all energy. The solid line is the trajectory when the energy dependence of the phase shift δ_f is not suppressed.

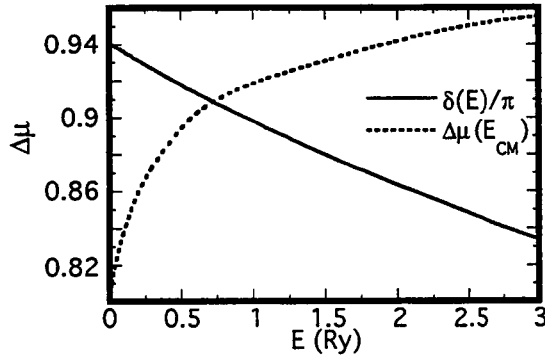


Figure 3-8: The intersection of $\delta_f(E)/\pi = \Delta\mu(E)$ and $\Delta\mu_f(E_{CM})$ predicting a Cooper minimum. Shown are calculation for $n = 5, l = 2 \rightarrow E, l' = 1$ transition. The intersection of these curves at $E = 0.72\text{Ry}$ corresponds to the Cooper minimum energy calculated for the transition when the phase shift varies naturally with energy.

minima, but the variation in phase shift must be taken into account and the Cooper minimum occurs where $\Delta\mu(E)$ curve and the $\Delta\mu_f(E_{CM})$ curve intersect.

3.2 Studies of Rydberg Atom Cooper Minima

In the previous section it was demonstrated that the difference in quantum defect $\Delta\mu$ between final and initial state was a significant determiner of the energy E_{CM} where a Cooper minimum would occur. All the prior calculations dealt with $n_i = 5$ initial states; yet, it is also important to study the effect of the initial state principle quantum number n_i on E_{CM} .

3.2.1 Movement of the Cooper minima for different n_i

Calculations of the energy E_{CM} at which Cooper minima occur for different initial n -states of a Rydberg series show that the energy of near threshold Cooper minima can be dependent on n_i .

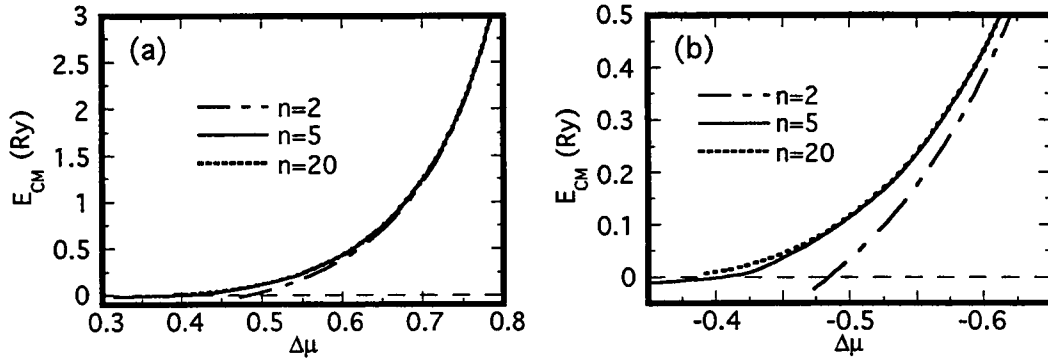


Figure 3-9: The energy E_{CM} of the Cooper minimum as a function of $\Delta\mu$ for $l \rightarrow l + 1$ transitions and different initial state principle quantum number. Shown are calculations for $n, l = 0 \rightarrow E, l' = 1$ transitions with $n = 2, 5, 20$ of hypothetical atoms for which $Z = 11$ and the initial $l = 0$ state is hydrogenic while the final $l' = 1$ state is a Schwinger function.

Shown in Figure 3-9 is a comparison of E_{CM} for a given $\Delta\mu$ of $l = 0 \rightarrow 1$ transitions of hypothetical $Z = 11$ atoms for initial states $n_i = 2, 5$, and 20 plotted as a function of $\Delta\mu$. As can be seen clearly in Figure 3-9(a), the energy of the Cooper minimum is roughly independent of n_i when the minimum occurs at higher energy (*i.e.* above 1 Rydberg). However, Figure 3-9(b) shows that for Cooper minima that occur in the near threshold region ($E < +0.5\text{Ry}$) there is a difference between the energy of the Cooper minima for $n_i = 2, 5$, and 20 at given $\Delta\mu$. In this case the energy dependence of μ_{n_i} was suppressed, thus all the difference in Cooper minimum energy is related only to n_i . Although no fit has been found that relates the shift in E_{CM} to n_i directly, one can observe that the difference between the $n = 2$ curve and the $n = 5$ curve is far greater than the difference between the $n = 5$ curve and the $n = 20$ curve. This indicates that $1/n$ is a more relevant quantity. In fact the dependence seems tied to the energy $E_i = 1/(n_i - \mu_i)^2$ of the initial state (in Rydbergs). As n_i increases, E_i becomes less negative and closer to the ionization threshold and seems

to push E_{CM} to higher energy. For example, consider the $\Delta\mu$ that causes a Cooper minimum at threshold, $\Delta\mu(0)$: for $n = 2$, $\Delta\mu(0) = 0.485$, for $n = 5$, $\Delta\mu(0) = 0.404$, and for $n = 20$, $\Delta\mu(0) = 0.368$. Or consider the E_{CM} of the three different initial states for $\Delta\mu = 0.52475$: for $n = 2$, $E_2 = -0.4595\text{Ry}$ gives $E_{CM} = 0.0961$; for $n = 5$, $E_5 = -0.0499\text{Ry}$ gives $E_{CM} = 0.16499$; for $n = 20$, $E_{20} = -0.00264\text{Ry}$ gives $E_{CM} = 0.16700$. Clearly the higher energies of the $n_i = 5$ and 20 states shifted the Cooper minimum to higher energy than the $n_i = 2$ state's Cooper minimum. For Cooper minima that occur at high energy ($E_{CM} \approx 3\text{Ry}$), the effect of n_i is quite small. For example, consider two transitions each with $\Delta\mu = 0.78462$, if the initial state is $n_i = 2$, then $E_{CM}(n_i = 2) = 2.9763\text{Ry}$, while for an $n_i = 20$ initial state we have $E_{CM}(n_i = 20) = 2.9991\text{Ry}$.

If the quantum defect μ_i of the initial state is allowed to vary naturally along the Rydberg series, one finds that for E_{CM} close to threshold, the higher E_i shifts the Cooper minimum higher in energy for a given $\Delta\mu$, just as in the fixed $\Delta\mu$ case shown in Figure 3-9. For Cooper minima far from threshold one finds that E_{CM} becomes essentially independent of n_i , yet, because μ_i varies slightly along a Rydberg series, the E_{CM} shifts in accordance with $\Delta\mu$ as discussed in section 3.1.1.

Examining the energy at which Cooper minima occur for $l = 1 \rightarrow 0$ transitions for different n_i -states reveals a similar situation. For near threshold Cooper minima the effect of n_i is strong, with the higher energy initial states shifting E_{CM} upward in energy. For Cooper minima far from threshold the initial state energy is insignificant. Figure 3-10 shows the near threshold region for $n_i, l = 1 \rightarrow E, l' = 0$ transitions with $n_i = 3, 5$ and 20 of hypothetical atoms for which $Z = 11$ and the initial $l = 0$ state is hydrogenic, while the final $l' = 1$ state is a Schwinger function. This graph shows the shift in E_{CM} that is dependent on the energy of the initial state for near threshold Cooper minima — note that only the Cooper minimum in the continuum

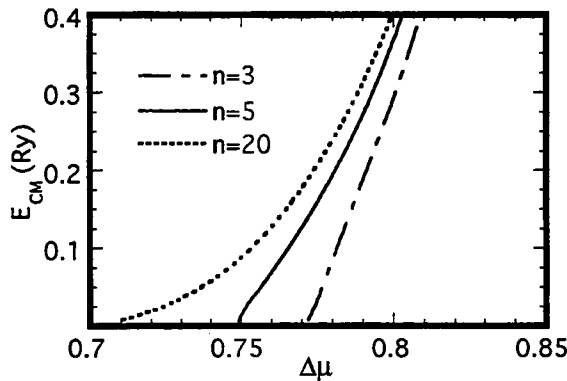


Figure 3-10: The energy E_{CM} of the Cooper minimum as a function of $\Delta\mu$ for $l \rightarrow l - 1$ transitions and different initial state principle quantum number. Shown are calculations for for $n, l = 1 \rightarrow E, l' = 0$ transitions with $n = 2, 5$, and 20 of hypothetical atoms for which $Z = 11$ and the initial $l = 0$ state is hydrogenic while the final $l' = 1$ state is a Schwinger function.

states is shown here because the Cooper minimum in the bound states can only be located approximately by interpolation from physical discrete bound states and thus the E_{CM} for bound states are only known approximately. Limited calculations seem to indicate that the lower energy Cooper minimum is also shifted to higher energy for higher initial state energy, possibly into the continuum. The shift into the continuum seems to occur for very high n_i ($n_i \approx 200$), and the shift is not high enough above threshold to bring the lower energy Cooper minimum into the region where the radial dipole matrix element's contour integral is less oscillatory and thus easier to evaluate. Cooper minima that occur far from the ionization threshold appear largely independent of n_i . The small variations in E_{CM} at high energies seem to correspond to small differences in $\Delta\mu$ as depicted in Figure 3-5.

3.2.2 Conditions for very near threshold Cooper minima for high Rydberg states

The previous section established the shift in Cooper minimum energy E_{CM} for near threshold due to the initial state's principle quantum number n_i . This section will study the inverse situation: what conditions are necessary to have a Cooper minimum at a fixed energy E_{CM} at or near threshold as n_i is increased. Specifically, this section will study the $\Delta\mu$ that generates a Cooper minimum near threshold as the initial state's energy is brought closer to E_{CM} .

For the $l \rightarrow l+1$ transitions, it is very convenient to use a Schwinger function for the initial state and a hydrogenic function for the final state. The use of a hydrogenic final state allows the use of the standard $E = 0$ limit of the continuum state hydrogen function. Using this $E = 0$ hydrogen wave function allows the convenient evaluation of the dipole matrix element at threshold for very high initial state principle quantum number, $n_i \sim 1000$.

Figure 3-11 shows the $\Delta\mu$ necessary to have a Cooper minimum at threshold for the entire Rydberg series of initial states for $l \rightarrow l+1$ transitions. The points are the actual calculated results, while the lines are least squares fits for the calculated values up to $n_i = 20$. The lines are a reasonable fit to the data through the $n_i = 20$ state as can be seen in Figure 3-11(a). However, Figure 3-11(b) shows that for very high Rydberg states there is significant deviation from the lower n_i data fit. The fitted lines extrapolate to a Cooper minimum for $n_i > 1000 \rightarrow E = 0$ threshold transitions at approximately $\Delta\mu = 0.35$. Even more interesting is the downward curvature of the actual calculated points as threshold is approached for $n_i > 50 \rightarrow E = 0$ threshold transitions, and that the calculations become essentially independent of l and seem to converge to $\Delta\mu \approx 0.334$. At such high n_i one might question the accuracy of the calculation; nonetheless, even at $n_i = 20$ the $l = 0 \rightarrow 1$ transitions are showing the

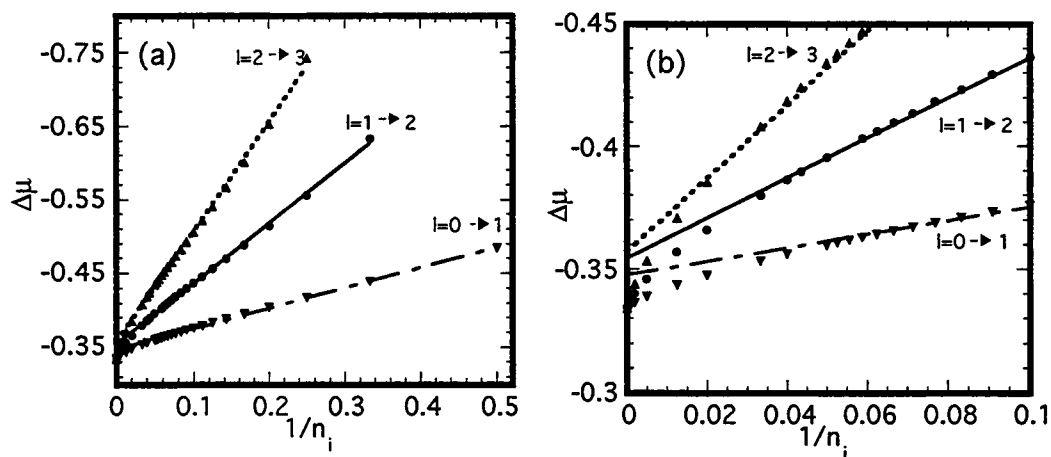


Figure 3-11: The $\Delta\mu$ necessary for a Cooper minimum at threshold as a function of $1/n_i$ for $l \rightarrow l+1$ transitions. Shown are the $l = 0 \rightarrow 1$, $l = 1 \rightarrow 2$, and $l = 2 \rightarrow 3$ transitions of hypothetical atoms for which $Z = 11$ and the initial state is a Schwinger function, while the final $l' = l+1$ state is hydrogenic. The data points show actual calculated points. The lines are least squares linear fits for the calculated values up to $n_i = 20$. (a) shows the entire Rydberg series of initial states. (b) shows the high Rydberg series.

beginning of this curve, and at $n_i = 20$ the calculation is certainly stable and reliable. The overall trend of decreasing $\Delta\mu$ as the energy of the initial state approaches the energy of the Cooper minimum (in this case threshold) seems to correspond to the pattern observed in Figure 3-3, where a $\Delta\mu < 0.32$ gave a Cooper minimum very close to the initial state's energy. Although no exact functional relationship has been determined, it seems that $\Delta\mu < 0.32$ gives a Cooper minimum close to the the initial state's energy regardless of n_i for $l \rightarrow l + 1$ transitions. It is also possible that as the energy difference $\Delta E_{CM,i} = E_{CM} - E_i$ between the initial state and the location of the Cooper minimum decreases toward zero, $\Delta\mu$ must also decrease to zero.

It should be noted that for a given $n_i, l \rightarrow E, l + 1$ transition one can predict whether the Cooper minimum is above or below threshold for a given set of parameters $(n_i, \Delta\mu)$. If the point $(n_i, \Delta\mu)$ is plotted on Figure 3-11 and lies above the relevant curve, then the Cooper minimum is in the continuum. If the point is below the relevant curve then the Cooper minimum is in the bound states.

The study of the $l \rightarrow l - 1$ Rydberg series for Cooper minima at the ionization threshold is more difficult. A Schwinger function must be used for the final state to get $\Delta\mu > 0$. The integrand in the radial dipole matrix becomes highly oscillatory for final state energies $E < 0.01$ when the final state is a Schwinger function; thus, some small positive energy in the continuum near threshold is chosen for the fixed E_{CM} value. The value used in the following calculations was $E_{CM} = 0.01\text{Ry}$. This energy was chosen because below this continuum energy the numerical integration of the radial dipole matrix element is less reliable. The numerical instability is a result of rapid oscillations of the final state's Schwinger wave function as $k \rightarrow 0$ near the $\rho = 0$ integration limit of Eq. 2.39. This numerical instability is especially prevalent for $l' = 0$ final Schwinger states. The fact that the Rydberg series limit is not the same energy as the E_{CM} does not allow a clean study of how $\Delta\mu$ changes in the limit

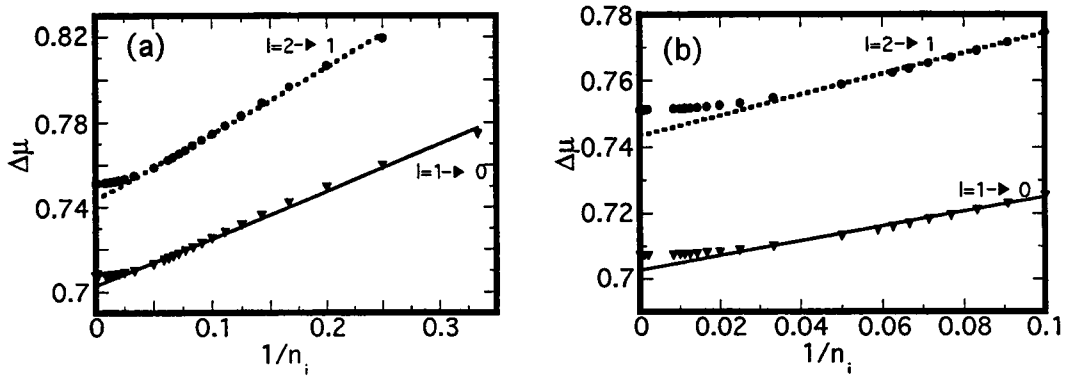


Figure 3-12: The $\Delta\mu$ necessary for a Cooper minimum at $E_{CM} = 0.01\text{Ry}$ as a function of $1/n_i$ for $l \rightarrow l-1$ transitions. Shown are the $l = 1 \rightarrow 0$, and $l = 2 \rightarrow 1$ transitions of hypothetical atoms for which $Z = 11$ and the initial state is hydrogenic, while the final $l' = l-1$ state is a Schwinger function. The data points show actual calculated points. The lines are least squares linear fits for the calculated values up to $n_i = 20$. (a) shows the entire Rydberg series of initial states, (b) shows the high Rydberg series.

as $E_i \rightarrow E_{CM}$. Fortunately, the use of a hydrogenic wave function for the initial state allows the whole Rydberg series to be examined.

The behavior of the Rydberg series of initial states $n_i, l = 1$, and $l = 2$ for $l \rightarrow l-1$ transitions is studied in Figure 3-12. The $\Delta\mu$ necessary for a Cooper minimum at the fixed $E_{CM} = 0.01\text{Ry}$ is plotted as a function of $1/n_i$. The curves show far less variation with l and appear almost parallel, unlike the $l \rightarrow l+1$ transitions shown in Figure 3-11.

The curves do not seem to converge to a single value for $n_i > 1000$. As can be seen in Figure 3-12(b), the linear least squares fit for $n_i < 20$ seems to give a reasonable approximation to the trend, except for $n_i > 50$. For $n_i > 50$ the curves seem to approach a fixed $\Delta\mu$, as the initial state approaches threshold and $\Delta E_{CM,i} = E_{CM} - E_i$ approaches 0.01Ry .

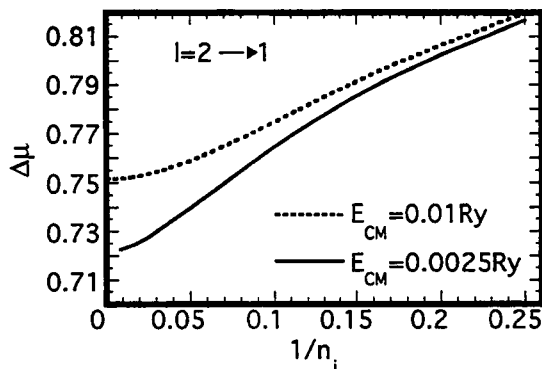


Figure 3-13: A comparison of the $\Delta\mu$ necessary for a Cooper minimum at $E_{CM} = 0.01\text{Ry}$ and $E_{CM} = 0.0025\text{Ry}$ as a function of $1/n_i$ for $l = 2 \rightarrow 1$ transitions. Note the stronger dependence of $\Delta\mu$ on $1/n_i$ for higher n_i , when the energy of the Cooper minimum is brought closer to threshold.

Calculations were performed for the $l = 2 \rightarrow 1$ series of transitions for $E_{CM} = 0.0025\text{Ry}$, and the results are shown in Figure 3-13. The curves show $\Delta\mu$ as a function of $1/n_i$ along with the results for the same transition series with $E_{CM} = 0.01\text{Ry}$. It is clearly seen that when the Cooper minimum is brought closer to threshold, the $\Delta\mu$ is more strongly dependent on $1/n_i$. In other words, when the Cooper minimum is brought closer in energy to the initial state, the difference in necessary quantum defects $\Delta\mu$ is decreased. The $E_{CM} = 0.0025\text{Ry}$ curve also shows the beginnings of approaching a fixed $\Delta\mu$ for $n_i > 100$, but the calculation becomes unstable for $n_i > 150$ so this trend can not be confirmed. The approach to a fixed $\Delta\mu$ occurs for $n_i > 50$ when $\Delta E_{CM,i} = E_{CM} - E_i = 0.01\text{Ry}$. However, for $\Delta E_{CM,i} = 0.0025$, the approach to a fixed $\Delta\mu$ occurs for $n_i > 100$. It is possible that the approach to a fixed $\Delta\mu$ is just an artifact of $\Delta E_{CM,i}$ approaching a fixed value greater than zero. If the calculation could be performed with the Cooper minimum at threshold, the fixed $\Delta\mu$ might not occur and the trend in $\Delta\mu$ might even turn radically downward, as it does for $l \rightarrow l + 1$ transitions. It is possible that the instabilities in the calculation

for the $E_{CM} = 0.0025\text{Ry}$ curve for $n_i > 150$ could be complicated by the presence of the second (bound state) Cooper minimum. Specifically, the lower energy Cooper minimum could get pushed up into the continuum, perhaps to an energy close to 0.0025Ry .

3.3 Applications and comparisons with other works

This section presents results of calculations intended to model physical systems for which there are experimental measurements and/or other calculations available. The results will be presented and discussed in light of the results given in prior sections.

There is one indirect calculation of the progression of Cooper minima for a Rydberg series of states done by J. Lahiri and S. Manson[22]. In their 1993 paper they calculate the cross section for bound-free transitions of lithium for a portion of the $l = 0$ Rydberg series of initial states. Figure 3-14 shows a comparison of photoionization cross sections for the lithium $l = 0$ Rydberg series of initial states ranging from $2s$ to $14s$. Figure 3-14(a) shows the Schwinger calculations of the theory presented in this dissertation. The parameters used in this calculation are the same as those used to generate the table of quantum defects given in Table 2.1. Figure 3-14(b) is a reproduction of a figure from J. Lahiri and S. Manson[22] showing the same physical system treated by Hartree-Slater calculations. Both calculations imply Cooper minima in the bound states. The agreement between the calculations is good, except for the region near the secondary maximum which occurs near threshold for the lithium $l = 0$ Rydberg series. The Schwinger calculations start at a larger value at threshold, and are more sharply peaked around the secondary maximum when compared to the Hartree-Slater calculations. Yet, for energies even 0.05Ry above threshold, the two calculations are extremely close, and if plotted together the Schwinger and Hartree-

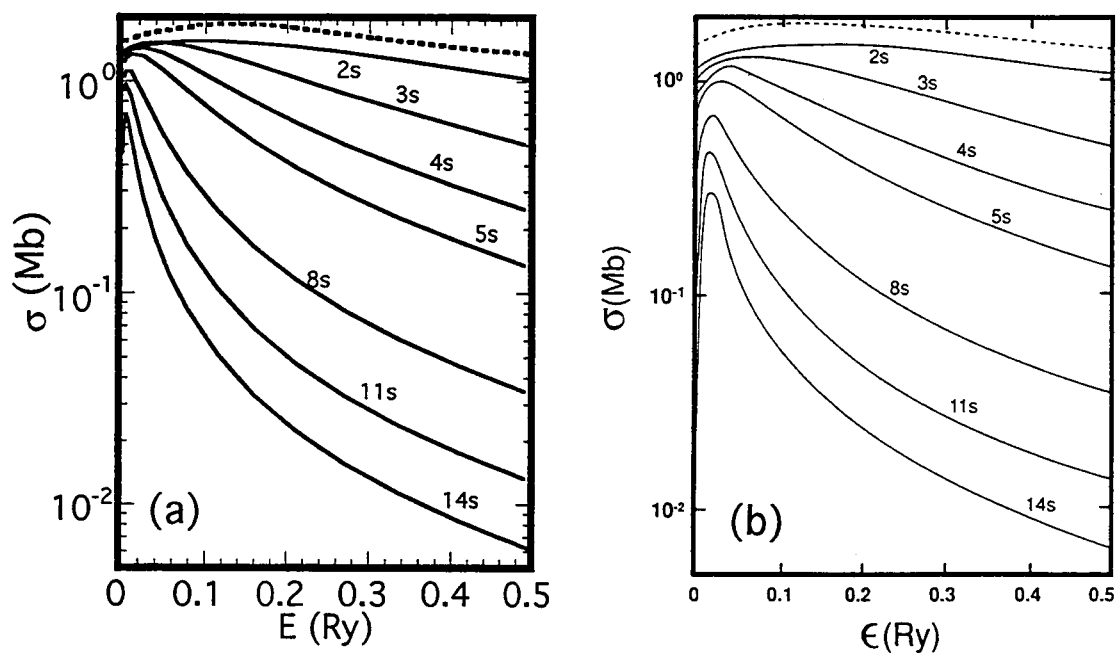


Figure 3-14: A comparison of photoionization cross sections for the lithium Rydberg series of initial states. (a) shows Schwinger calculations (present work), (b) shows Hartree-Slater calculations. Both sets of calculations imply Cooper minima in the bound states. [Source for (b): J. Lahiri and S. T. Manson, Phys. Rev. A 48, 3674 (1993)].

Slater calculations would be almost indistinguishable above 0.05Ry. The disagreement between the Schwinger and Hartree-Slater calculations could be due to differences in the predicted locations of the Cooper minima, or differences in the shape of the cross sections near the Cooper minima. It is likely that minor differences in location and shape are responsible for the differences in the photoionization cross sections shown. Further, it is known that the Hartree-Slater theory gives reasonably good quantum defects, yet the results are not a perfect match to the data as was noted in the lithium 2s wave functions shown in Figure 2-3. It has been shown in the work presented here that small differences in the $\Delta\mu$ for the transition can shift the energy of the Cooper minimum on the scale of Figure 3-14, so the question of accuracy can only be resolved by experimentation. Of course the Hartree-Slater theory is a more satisfying theory because it is *ab initio* while the Schwinger theory requires some input from experiment, namely the quantum defect (phase shift) at threshold.

Figure 3-15 shows a sample of the cross sections in Figure 3-14 extended to include the bound-bound transitions. These graphs show the approximate locations of the Cooper minima, and demonstrate how the energy of the Cooper minimum is pushed upward as the principle quantum number n_i of the initial state is increased. The quantum defect difference $\Delta\mu$ also changes slightly as n_i increases. The μ of each initial state is $\mu_{2s} = 0.4103$, $\mu_{5s} = 0.4015$, and $\mu_{14s} = 0.4001$, which amounts to a difference of -0.0102 in $\Delta\mu$ between $2s \rightarrow E,p$ transitions and the $14s \rightarrow E,p$ transitions. This degree of variation in $\Delta\mu$ is small. In this case the shift associated with the n_i of the initial state is the dominant effect which pushes the Cooper minimum to higher energy, while the less negative $\Delta\mu$ for the higher n_i transitions should shift the Cooper minimum very slightly down in energy.

It is interesting to note that the extremely high Rydberg series of lithium has quantum defects such that $\Delta\mu = 0.3527$ for a transition from $n_i \sim 1000, l = 0 \rightarrow$

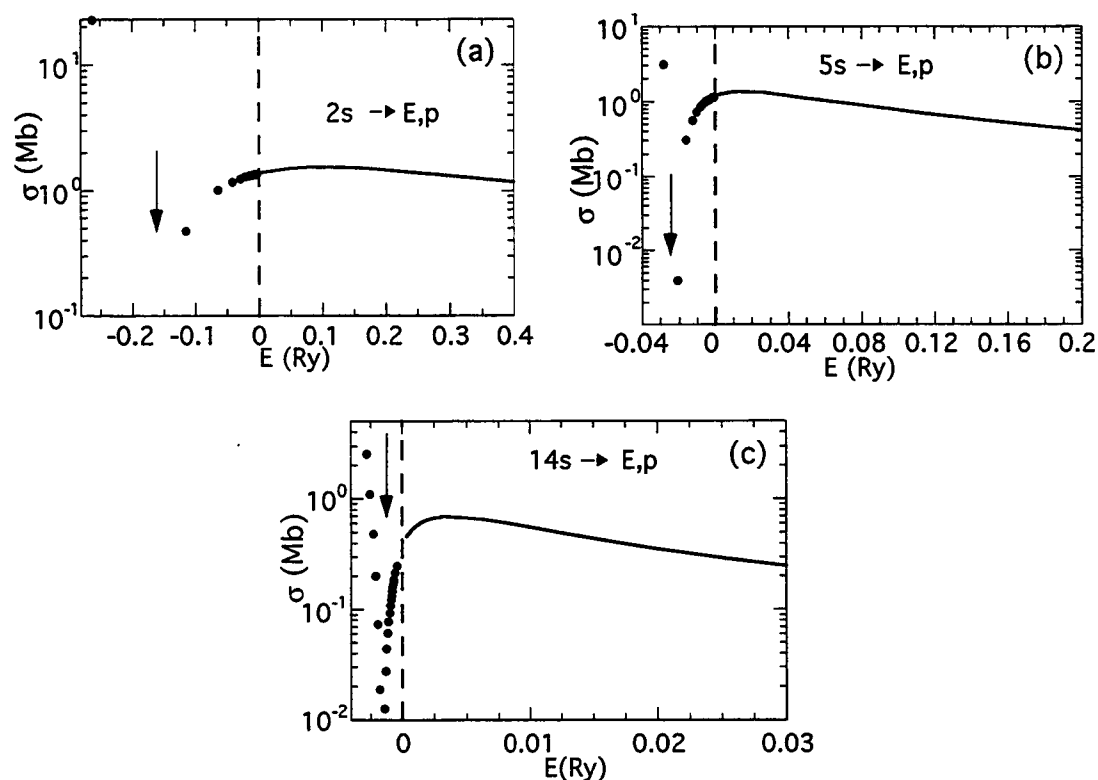


Figure 3-15: The bound-bound and bound-free photo-excitation cross sections for a sample of the lithium Rydberg series initial states. These figures show bound-bound portion of the spectrum for which only bound-free portion was shown in Figure 3-14(a). The arrow on each graph shows the approximate location of the Cooper minimum in the bound-bound transitions.

$E \approx 0, l' = 1$; thus the lithium atom is a physical system for which the results of Figure 3-11 could be tested. If the Cooper minimum for the $n_i \sim 1000, l = 0 \rightarrow E, l' = 1$ transitions is at threshold, the straight line extrapolations from lower n_i would be correct; however, if the Cooper minimum moves into the continuum it would be evidence in favor of the downward curve in Figure 3-11(b) that is necessary to keep the Cooper minimum at threshold. Admittedly, these suggested experiments would be a supreme challenge; notwithstanding, there is one measurement for photoionization of lithium 23s[45] that shows a Cooper minimum at $n = 50$ by showing that photoionization of Li 23s is more likely to proceed via a 4, 6, or even 8 photon process than by the 2 photon process that goes through the $n = 50$ intermediate state. The Floquet calculations used in that paper show a Cooper minimum between the 50p and 51p states. For the Schwinger theory the $23s \rightarrow 50p$ should have $\Delta\mu = -0.3527$, and an examination of Figure 3-11(b) for the $l = 0 \rightarrow 1$ reveals that $\Delta\mu = -0.3581$ yields a Cooper minimum at threshold, so the $\Delta\mu = -0.3527$ should give a Cooper minimum in the bound states, which corresponds with the experimental evidence. Full Schwinger calculations were attempted for lithium $23s \rightarrow 50p$ and higher states, unfortunately, the calculation became numerically unstable around $n_f = 50$ when Schwinger wave functions were used for both initial and final states because of the highly oscillatory integrand for the two high Rydberg states. Another distinct possibility is that the Cooper minimum is present here and the integration fails to converge because a highly oscillatory integrand should integrate to zero, but numerical error prevents convergence. Yet, as was shown in Figure 3-6 as long as the $\Delta\mu$ is correct, using a Schwinger function for the initial state and a hydrogenic function for the final state is an excellent approximation. This approximation should calculate the location of the Cooper minimum slightly too high in energy; but, this error should be very small since the 50p state has $\mu = 0.0471$, which is not that different from hydrogenic.

Direct calculations with an initial Schwinger state with $\mu = 0.3526$ and a final hydrogenic state show a Cooper minimum between the $51p$ and $52p$ state which is in very good agreement with the experiment.

The case of the sodium $4d \rightarrow \epsilon p$ transitions presents another example where the Schwinger theory can be applied. Msezane, Lahiri, and Manson[20] show Hartree-Slater, and Hartree-Fock (velocity and length form) calculations for this $l \rightarrow l - 1$ transition. Their figure is reproduced in Figure 3-16(b) and contains an arrow that points to a single experimental data point[46] at approximately 0.025Ry where the cross section for this sodium transition was “too small for the experiment to see, $< 0.1\text{Mb}$ ”. The Schwinger calculation for $\mu_{4d} = 0.008657$ and threshold $\mu_{l=1} = 0.85496$, both with screened potential parameter $c = 2.3115$, is shown in Figure 3-16(a). The $\Delta\mu = 0.8463$ for the Schwinger calculation is slightly too large compared to the experimental value of $\Delta\mu = 0.8426$, so the location of the Schwinger calculated Cooper minimum is expected to be at a slightly higher energy than the experimental value. At the energy location of the arrow ($E \approx 0.025\text{Ry}$) in Figure 3-16(b), the Schwinger cross section is approximately 0.005Mb , which is within the bounds set by the experimental data point. This comparison shows the Schwinger result closer to the Hartree-Fock results than the Hartree-Slater results.

Figure 3-16 shows one reason for the frustration of both theorists and experimentalist working on Cooper minima — predictions of Cooper minima can vary widely, and may not be accurate. In Figure 3-16(b) the Hartree-Slater and Hartree-Fock Cooper minima differ by about 0.11Ry or about 1.5eV . This is not a large difference in E_{CM} , but it can be enough to complicate an experimental search for a theoretical prediction. Since the work presented here shows the quantum defect (phase shift) difference is the major determiner of Cooper minimum location, the first question to

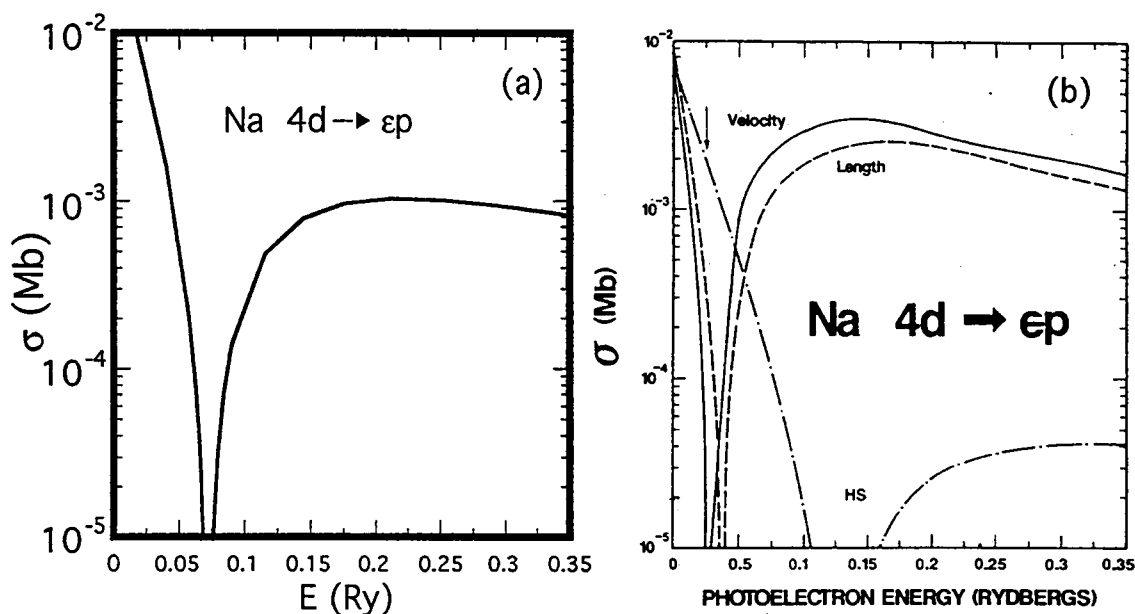


Figure 3-16: The bound-free photo-excitation cross sections for sodium $4d \rightarrow \epsilon p$ transitions. (a) shows the Schwinger calculation with $\Delta\mu = 0.8463$. (b) a reproduction of a graph from Msezane, Lahiri, and Manson[20] showing 3 different calculations; Hartree-slater (HS), Hartree-Fock velocity form (Velocity), and Hartree-Fock length form (Length). Note the typographical error in (b) — the second label on the horizontal axis should be 0.05, (not 0.5). [Sorce for (b): A.Z.Msezane, J. Lahiri and S. T. Manson, Phys. Rev. A **33**, 4406 (1986)].

ask of any Cooper minimum prediction is "how accurate are the quantum defects?" Asking this question may help distinguish between "general trend" predictions and Cooper minima that are likely to be found experimentally.

Chapter 4

Conclusions

This thesis has presented simple method for studying Cooper minima in the dipole matrix elements of valence electrons of multi-electron atoms. This method has proven useful for the study of high Rydberg states and the Cooper minima of these states. The method uses wave functions derived using Schwinger's variational theory for a screened Coulomb potential. These wave functions are analytic integral expressions that show the explicit dependence of the functions on the quantum defect. The Schwinger functions can be cast in a form that closely resembles the functional form of the hydrogenic wave functions, and the Schwinger functions become hydrogenic in the limit of zero quantum defect. As such, these wave functions are a generalization of the hydrogenic functions that include the quantum defect explicitly, but do not include other effects. The Schwinger wave functions compare quite favorably to numerical Hartree-Slater wave functions. This explicit inclusion of the quantum defect, while ignoring other aspects of electrons in multi-electron atoms, makes these wave functions uniquely useful for studying Rydberg electrons. The radial dipole matrix elements derived herein are reduced to one contour integral on finite limits that can be evaluated easily on desk top computational platforms like a MacintoshTM computer

with MathematicaTM installed; thus the limited computational aspects of this theory are highly accessible.

The energy E_{CM} at which a Cooper minimum occurs in the photo-excitation spectrum as a function of the difference in quantum defects $\Delta\mu = \mu_f - \mu_i$ for an atom was studied for both $l \rightarrow l + 1$ and $l \rightarrow l - 1$ transitions. For $l \rightarrow l + 1$ transitions it was clearly demonstrated that the Cooper minimum first appears in the bound-bound transitions close to the first transition energy for very small negative $\Delta\mu$. As $\Delta\mu$ is made more negative, the Cooper minimum moves up through the bound-bound transitions and into the bound-free transitions where it continues to move higher in energy as $\Delta\mu \rightarrow -1$. This trend was explicitly detailed Figure 3-3 for the $l = 0 \rightarrow 1$, $l = 1 \rightarrow 2$, and $l = 2 \rightarrow 3$ transitions. This figure is a useful guide for predicting the energy E_{CM} at which a Cooper minimum occurs given the quantum defect difference $\Delta\mu$ of the transition.

For the $l \rightarrow l - 1$ transitions the Cooper minimum behaves quite differently. For these transitions the Cooper minimum appears in the near threshold region for $\Delta\mu > 0.7$ and the Cooper minimum seems to bifurcate into two Cooper minima. One Cooper minimum moves higher in energy as $\Delta\mu$ increases, while the other Cooper minimum moves down through the Rydberg series of bound states and is soon lost below the initial state's energy. This unusual behavior of bifurcation of Cooper minima near threshold and migration of the lower energy Cooper minimum below the initial bound state, shown in Figure 3-5, occurs in the very small span of $0.75 < \Delta\mu < 0.78$ for the $l = 1 \rightarrow 0$ transitions, and occurs in an even smaller range for $l = 2 \rightarrow 1$ transitions. Because of this limited range in $\Delta\mu$ of bifurcated double Cooper minima it is unlikely that this effect could be observed in the physical atomic systems that exist in nature. As such, the lower energy Cooper minimum will probably remain an interesting theoretical construct only.

The results in Figure 3-3 and Figure 3-5 are the first direct evidence of a quantitative relationship between $\Delta\mu$ and E_{CM} . Such a relationship has been alluded to in the literature before, but this work is the most complete and coherent quantitative study of the connection between $\Delta\mu$ and E_{CM} . This study demonstrated the fundamental similarity of the trajectory of Cooper minima for all $l \rightarrow l+1$ transitions. The Cooper minima of all $l \rightarrow l-1$ transitions are also fundamentally similar. However, there is a large qualitative difference between the Cooper minima of $l \rightarrow l+1$ and $l \rightarrow l-1$ transitions.

The dependence of E_{CM} on the principle quantum number n_i for a Rydberg series of initial states was also studied. This study showed that n_i has no appreciable effect on Cooper minima that occur far from threshold. However, when the Cooper minimum occurs at or near threshold, E_{CM} is pushed upward as n_i is increased. Figure 3-11 provides a guide for determining if a Cooper minimum will occur in the bound-bound transitions or in the bound-free transitions for $l \rightarrow l+1$ transitions. Given the initial state's n_i , l_i and μ_i , and the final state's $l_f = l_i + 1$ and threshold μ_f , Figure 3-11 quickly determines whether the Cooper minimum is to be found in the bound-bound or bound-free transitions.

Unfortunately, numerical instabilities of the very near threshold model calculations did not permit a clean study of Cooper minima at threshold for $l \rightarrow l-1$ transitions. As a result no convenient guide (like Figure 3-11 for $l \rightarrow l+1$) to near threshold Cooper minimum location could be determined for $l \rightarrow l-1$.

These studies of Cooper minima for an entire Rydberg series of initial states are a new and unique feature of this work. Using this theory one can calculate cross sections and radial dipole matrix elements for transitions involving states with principle quantum numbers as high as $n = 50$, and in some cases calculations can be performed with $n > 1000$.

When the methodology developed in this work was applied to physically measured and measurable systems, the results were favorable. The study of the Rydberg series for lithium showed good confirmation of the results, and showed that this study is a good framework in which to interpret Cooper minimum results. A calculation of the sodium $4d \rightarrow \epsilon p$ transition showed a Cooper minimum that agreed fairly well with Hartree-Fock calculations of the same, and was consistent with the one experimental data point available.

Overall it was found that the difference in quantum defect is the single greatest determiner of the energy at which a Cooper minimum occurs. Figure 3-3 and Figure 3-5 prove a guide to locating Cooper minima based on the quantum defect difference $\Delta\mu = \mu_f - \mu_i$ of initial and final states. This study also underscored the need for theoretical calculations to accurately represent the quantum defects of the wave functions in Cooper minimum calculations.

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APPENDICES

Appendix A

A derivation of $\langle \vec{r} | G_l V | F_l \rangle$

This Appendix will derive $G_l V | F_l \rangle$ in coordinate space directly.

$G_l V | F_l \rangle$ was first derived by Kelsey and Macek[47] in momentum space for

$$V = e^{i\vec{p}_1 \cdot \vec{r}} \quad \text{and} \quad |F_l\rangle = e^{-u_1 r} \quad (\text{A.1})$$

In Maleki's work[33], $G_l V | F_l \rangle$ in coordinate space is derived from Kelsey and Macek Eq. (22) by

$$\lim_{P \rightarrow 0} \left\{ \frac{1}{P_l} \int_{-1}^1 \chi(\vec{p}_1, \vec{r}) P(\cos \theta) d(\cos \theta) \right\} \quad (\text{A.2})$$

where $\chi(\vec{p}_1, \vec{r}) = \langle \vec{p}_1 | G_l V | F_l \rangle$.

The coordinate representation of $G_l V | F_l \rangle$ is derived below directly in a manor that mirrors the derivation of $G_l V | F_l \rangle$ in momentum space given by Kelsey and Macek[47].

The function $G_l V | F_l \rangle$ is a solution to an inhomogeneous Schrödinger equation:

$$[H - \varepsilon] \mathcal{R} = -V | F_l \rangle \quad (\text{A.3})$$

where H is the hydrogenic hamiltonian, ε is the energy, $\mathcal{R}$ is the radial wave function, $V = \lambda e^{-cr}/r$ is the potential of the core, and $|F_l\rangle = r^l e^{-b_1 r}$.

With $X^2 = \sqrt{-2\varepsilon}$ we have

$$-\frac{1}{2} \frac{1}{r} \frac{d^2}{dr^2} (r\mathcal{R}) + \left[\frac{l(l+1)}{2r^2} - \frac{\gamma}{r} + \frac{1}{2} X^2 \right] \mathcal{R} = -\lambda r^{l-1} e^{-(b_l+c)r} \quad (\text{A.4})$$

where γ is the asymptotic charge of the core.

Now let $\mathcal{R} = \frac{1}{r} \mathcal{X}$, and multiply by $-2r$ to get

$$\frac{d^2}{dr^2} \mathcal{X} - \frac{l(l+1)}{r^2} \mathcal{X} + \frac{2\gamma}{r} \mathcal{X} - X^2 \mathcal{X} = 2\lambda r^l e^{-(b_l+c)r} \quad (\text{A.5})$$

Define $\zeta = -iXr$, and divide by $-X^2$ yielding

$$\frac{d^2}{d\zeta^2} \mathcal{X} + \left[1 + \frac{i2\gamma}{X\zeta} - \frac{l(l+1)}{\zeta^2} \right] \mathcal{X} = -\frac{2\lambda(i)^l}{X^{l+2}} \zeta^l e^{-i\frac{(b_l+c)}{X}\zeta} \quad (\text{A.6})$$

Now one can observe that the left side of this equation is the Coulomb wave differential equation [see Ref. [44], Eq. (14.1.3)] whose homogeneous solution in terms of confluent hypergeometric functions can be written in terms of $L_{(n)}^{(\alpha)}$, a generalized Laguerre function,

$$F_l(-i\frac{\gamma}{X}, \zeta) = C_l(-i\frac{\gamma}{X}) \frac{(2l+1)!(\frac{\gamma}{X} - l - 1)!}{(\frac{\gamma}{X} + l)!} \zeta^{l+1} e^{-i\zeta} L_{(\frac{\gamma}{X}-l-1)}^{(2l+1)}(2i\zeta) \quad (\text{A.7})$$

So going back to the inhomogeneous differential equation, several transformations can get the equation soluble in generalized Laguerre polynomials. First, let $\tau = \frac{\gamma}{X}$, and $\mathcal{X} = \zeta^{l+1} \mathcal{X}^{(a)}$; then divide by ζ^l to get

$$\zeta \frac{d^2 \mathcal{X}^{(a)}}{d\zeta^2} + 2(l+1) \frac{d\mathcal{X}^{(a)}}{d\zeta} + [\zeta + 2i\tau] \mathcal{X}^{(a)} = \frac{-2\lambda(i)^l}{X^{l+2}} \exp \left[-i \frac{(b_l+c)}{X} \zeta \right] \quad (\text{A.8})$$

Now let $\mathcal{X}^{(a)} = \exp(-i\zeta) \mathcal{X}^{(b)}$, then multiply the differential equation by $\exp(i\zeta)$, and set $\nu = 2i\zeta$. Division by $2i$ leads to the following form

$$\nu \frac{d^2 \mathcal{X}^{(b)}}{d\nu^2} + [2(l+1) - \nu] \frac{d\mathcal{X}^{(b)}}{d\nu} + [\tau - (l+1)] \mathcal{X}^{(b)} = \frac{\lambda(i)^{l+1}}{X^{l+2}} \exp \left[\frac{1}{2} \left(1 - \frac{(b_l+c)}{X} \right) \nu \right] \quad (\text{A.9})$$

Note the similarity between the left side and the generalized Laguerre differential equation [Ref. [44], Eq. (22.6.15)]

$$x \frac{d^2}{dx^2} L_j^\alpha(x) + [\alpha + 1 - x] \frac{d}{dx} L_j^\alpha(x) + j L_j^\alpha(x) = 0 \quad (\text{A.10})$$

if $\alpha + 1 = 2(l + 1)$ and $j = \tau - (l + 1)$.

Also note that the right hand side of Eq. (A.9) can be put in the form of the Laguerre generating function [See Ref. [44], Eq. (22.9.15)] with a parameter change

$$\frac{1}{2} \left(1 - \frac{(b_l + c)}{X} \right) = \frac{s}{s - 1}$$

thus: $s = \frac{-X + b_l + c}{X + b_l + c} = -D$ (A.11)

$$\text{so that: } \exp \left[\frac{s}{s - 1} \nu \right] = (1 - s)^{2l+2} \sum_{j=0}^{\infty} s^j L_j^{2l+2}(\nu) \quad (\text{A.12})$$

So, the full differential equation can be written as

$$\nu \frac{d^2 \mathcal{X}^{(b)}}{d\nu^2} + [2(l + 1) - \nu] \frac{d\mathcal{X}^{(b)}}{d\nu} + [\tau - (l + 1)] \mathcal{X}^{(b)} = \frac{\lambda(i)^{l+1}}{X^{l+2}} (1 - s)^{2l+2} \sum_{j=0}^{\infty} s^j L_j^{2l+2}(\nu) \quad (\text{A.13})$$

and one can attempt a solution in terms of a sum of Laguerre polynomials. It will be shown that the desired solution is

$$\mathcal{X}^{(b)} = \frac{\lambda(i)^{l+1}}{X^{l+2}} (1 - s)^{2l+2} \sum_{j=0}^{\infty} \frac{s^j}{(j - \tau + l + 1)} L_j^{2l+2}(\nu) \quad (\text{A.14})$$

To show the above solution works, insert the solution in the full differential equation Eq. (A.13). This gives

$$\begin{aligned} & \frac{\lambda(i)^{l+1}}{X^{l+2}} (1 - s)^{2l+2} \left\{ \nu \sum_{j=0}^{\infty} \frac{s^j}{(j - \tau + l + 1)} \frac{d^2}{d\nu^2} L_j^{2l+2}(\nu) \right. \\ & + [2(l + 1) - \nu] \sum_{j=0}^{\infty} \frac{s^j}{(j - \tau + l + 1)} \frac{d}{d\nu} L_j^{2l+2}(\nu) \\ & \left. + [\tau - (l + 1)] \sum_{j=0}^{\infty} \frac{s^j}{[j - \tau + (l + 1)]} L_j^{2l+2}(\nu) \right\} = \\ & \frac{\lambda(i)^{l+1}}{X^{l+2}} (1 - s)^{2l+2} \sum_{j=0}^{\infty} s^j L_j^{2l+2}(\nu) \end{aligned} \quad (\text{A.15})$$

The solution $\mathcal{X}^{(b)}$ is of course a solution of the Laguerre differential equation

$$\begin{aligned} \frac{\lambda(i)^{l+1}}{X^{l+2}} (1-s)^{2l+2} \left\{ \nu \sum_{j=0}^{\infty} \frac{s^j}{(j-\tau+l+1)} \frac{d^2}{d\nu^2} L_j^{2l+1}(\nu) \right. \\ + [(2l+1)+1-\nu] \sum_{j=0}^{\infty} \frac{s^j}{(j-\tau+l+1)} \frac{d}{d\nu} L_j^{2l+1}(\nu) \\ \left. + \sum_{j=0}^{\infty} \frac{s^j}{(j-\tau+l+1)} j L_j^{2l+1}(\nu) \right\} = 0 \end{aligned} \quad (\text{A.16})$$

because it is a sum of Laguerre polynomials multiplied by some factors.

Now if the above Laguerre differential equation Eq. (A.16) is subtracted from the inhomogeneous differential equation Eq. (A.15) we find

$$\begin{aligned} \frac{\lambda(i)^{l+1}}{X^{l+2}} (1-s)^{2l+2} \left\{ \sum_{j=0}^{\infty} [j-\tau+(l+1)] \frac{s^j}{[j-\tau+(l+1)]} L_j^{2l+2}(\nu) \right\} = \\ \frac{\lambda(i)^{l+1}}{X^{l+2}} (1-s)^{2l+2} \sum_{j=0}^{\infty} s^j L_j^{2l+2}(\nu) \end{aligned} \quad (\text{A.17})$$

So the attempted $\mathcal{X}^{(b)}$ is indeed the solution of the inhomogeneous Schrödinger equation.

Now note the following:

$$\frac{1}{(j-\tau+l+1)} = \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \int_c d\rho \rho^{-\tau+l+j} \quad (\text{A.18})$$

where the contour is given in Figure A-1. So $\mathcal{X}^{(b)}$ can be rewritten as

$$\mathcal{X}^{(b)} = \frac{\lambda(i)^{l+1}}{X^{l+2}} (1-s)^{2l+2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \int_c d\rho \rho^{-\tau+l} \sum_{j=0}^{\infty} (sj)^j L_j^{2l+2}(\nu) \quad (\text{A.19})$$

and the summation above can be rewritten with the help of the Laguerre generating function [Ref. [44], Eq. (22.9.15)] such that

$$\sum_{j=0}^{\infty} (sj)^j L_j^{2l+2}(\nu) = (1-s\rho)^{-2l-2} \exp \left[\frac{s\rho}{(s\rho-1)} \right] \quad (\text{A.20})$$

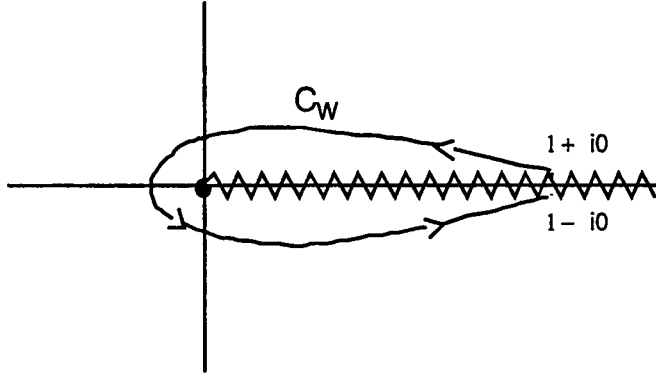


Figure A-1: The integration contour for $G_l V|F_l\rangle$. Shown are the pole at $w = 0$, the branch cut ($0 \rightarrow +\infty$), and the contour limits of $1 \pm i0$.

and $\mathcal{X}^{(b)}$ becomes

$$\begin{aligned} \mathcal{X}^{(b)} = & -\frac{\lambda(i)^{l-1}}{X^{l+2}}(1-s)^{2l+2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\ & \times \int_c d\rho \rho^{-\tau+l}(1-s\rho)^{-2l-2} \exp \left[\frac{s\rho}{(s\rho-1)} \right] \end{aligned} \quad (\text{A.21})$$

Now if all the function and variable transformation are reversed one gets

$$\begin{aligned} \mathcal{R} = & \lambda 4^{l+1} r^l X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\ & \times \int_c d\rho \rho^{-\tau+l} (D\rho + 1)^{-2l-2} \exp \left[Xr \frac{(D\rho - 1)}{(D\rho + 1)} \right] \end{aligned} \quad (\text{A.22})$$

and with $\mathcal{R} = rG_l V|F_l\rangle$ we have the form given earlier in Chapter 2, Eq. 2.38

$$\begin{aligned} G_l V|F_l\rangle = & \lambda(4r)^{l+1} X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\ & \times \int_c d\rho \rho^{-\tau+l} (D\rho + 1)^{-2l-2} \exp \left[Xr \frac{(D\rho - 1)}{(D\rho + 1)} \right]. \end{aligned} \quad (\text{A.23})$$

Appendix B

Continuity of the wave functions across threshold

This appendix will show that the bound and continuum wave functions are continuous across threshold.

The continuity of wave functions across threshold is essential for a theory to be credible, this condition is express in the following statement:

$$\begin{aligned} \lim_{E_n \rightarrow 0^-} |P_{n,l}\rangle \tau^{3/2} &= \lim_{\epsilon \rightarrow 0^+} |P_{\epsilon,l}\rangle \\ \lim_{E_n \rightarrow 0^-} \left\{ G_l V |F_l\rangle \frac{\tau^{3/2}}{N} \right\} &= \\ \lim_{\epsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} \left(e^{-i\delta_l} |f_l\rangle + \frac{\sin(\delta_l)}{\langle f_l | V | F_l \rangle} G_l(-X) V |F_l\rangle \right) \right\} \end{aligned} \quad (\text{B.1})$$

where $\tau^{3/2} = (n - \mu)^{3/2}$ was added to change the bound state normalization from "unity" to "unit energy" to correspond with the continuum state normalization.

The first step in this proof is to write the bound state in terms of $G(-X)$. Note that the principle valued Greens function can be expressed as

$$G_l^{(P)} = \frac{1}{2}(G_l(X) + G_l(-X)) \quad (\text{B.2})$$

also as

$$G_l^{(P)} = G_l(X) + i|f_l\rangle\langle f_l| \quad (\text{B.3})$$

So one finds

$$G_l(X) = G(-X) + 2i|f_l\rangle\langle f_l|. \quad (\text{B.4})$$

And the continuity condition becomes

$$\begin{aligned} \lim_{E_n \rightarrow 0^-} \left\{ G_l(-X)V|F_l\rangle \frac{\tau^{3/2}}{N} + 2i|f_l\rangle\langle f_l|V|F_l\rangle \frac{\tau^{3/2}}{N} \right\} = \\ \lim_{\epsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} \left(e^{-i\delta_l} |f_l\rangle + \frac{\sin(\delta_l)}{\langle f_l|V|F_l\rangle} G_l(-X)V|F_l\rangle \right) \right\} \end{aligned} \quad (\text{B.5})$$

where $-X \leftrightarrow +ik$ in continuation across threshold.

The continuation proof now breaks into two parts:

Condition #1

$$\lim_{E_n \rightarrow 0^-} \left\{ G_l(-X)V|F_l\rangle \frac{\tau^{3/2}}{N} \right\} = \lim_{\epsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} \frac{\sin(\delta_l)}{\langle f_l|V|F_l\rangle} G_l(-X)V|F_l\rangle \right\} \quad (\text{B.6})$$

and

Condition #2

$$\lim_{E_n \rightarrow 0^-} \left\{ 2i|f_l\rangle\langle f_l|V|F_l\rangle \frac{\tau^{3/2}}{N} \right\} = \lim_{\epsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} (e^{-i\delta_l} |f_l\rangle) \right\}. \quad (\text{B.7})$$

Treating Condition #1 first; it is easily seen that the $G_l(-X)V|F_l\rangle$ factor of Eq. B.6 is continuous across threshold because the Coulomb Greens function $G(-X)$ continues across threshold while the V and $|F_l\rangle$ are identical above and below threshold. So the continuation question in Eq. B.6 becomes

$$\lim_{E_n \rightarrow 0^-} \frac{\tau^{3/2}}{N} \stackrel{?}{=} \lim_{\epsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} \frac{\sin(\delta_l)}{\langle f_l|V|F_l\rangle} \right\} \quad (\text{B.8})$$

It can be shown that

$$\lim_{E_n \rightarrow 0^-} N = \frac{\lambda(2\gamma)^{l+1} \exp\left(-\frac{2\gamma}{b+c}\right) \pi \tau^{3/2}}{(b+c)^{2l+2} \sin(\pi\mu)} \quad (\text{B.9})$$

and

$$\lim_{\varepsilon \rightarrow 0^+} \langle f_l | V | F_l \rangle = \frac{\lambda \sqrt{\pi} (2\gamma)^{l+1} \exp\left(-\frac{2\gamma}{b+c}\right)}{(b+c)^{2l+2}}. \quad (\text{B.10})$$

Inserting these limits into Eq. B.8 one finds

$$\frac{(b+c)^{2l+2} \sin(\pi\mu)}{\lambda \gamma^{l-1/2} 2^{l+1} \exp\left(-\frac{2\gamma}{b+c}\right) \pi} \longleftrightarrow \frac{(b+c)^{2l+2} \sin(\delta)}{\lambda \gamma^{l-1/2} 2^{l+1} \exp\left(-\frac{2\gamma}{b+c}\right) \pi} \quad (\text{B.11})$$

with the condition from quantum defect theory[16]

$$\lim_{E_n \rightarrow 0^-} \pi\mu = \lim_{\varepsilon \rightarrow 0^+} \delta(\varepsilon). \quad (\text{B.12})$$

So Condition #1 of Eq. B.6 is true and the terms of the wave functions that contain $G_l(-X)V|F_l\rangle$ continue smoothly across threshold.

Now treating Condition #2 of Eq. B.7; first note that the Coulomb wave function $|f_l\rangle$ is continuous across threshold; so the question in Eq. B.7 becomes

$$\lim_{E_n \rightarrow 0^-} \left\{ 2i \langle f_l | V | F_l \rangle \frac{\tau^{3/2}}{N} \right\} \stackrel{?}{=} \lim_{\varepsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} \left(e^{-i\delta_l} \right) \right\}. \quad (\text{B.13})$$

With the limits given above for N and $\langle f_l | V | F_l \rangle$, and re-writing the $\sin(\pi\tau)$ in terms of exponentials one finds

$$\lim_{E_n \rightarrow 0^-} \left\{ \frac{1}{\sqrt{\pi}} e^{-i\pi\mu} \right\} = \lim_{\varepsilon \rightarrow 0^+} \left\{ \frac{1}{\sqrt{\pi}} \left(e^{-i\delta_l} \right) \right\}. \quad (\text{B.14})$$

Again noting the relation between quantum defect and phase shift one sees that Condition #2 of Eq. B.7 is also satisfied.

Thus it is proven that the bound state wave function and the continuum state wave function are continuous across the ionization threshold as they must be for the theory to be credible.

Appendix C

A list of matrix elements

This Appendix is a list of important matrix elements that are evaluated in closed form in Ref. [33, 34] and some important limits of those matrix elements.

$$\langle F_l | V | F_l \rangle = \frac{\lambda(2l+1)!}{(2b_l+1)^{2l+2}} \quad (\text{C.1})$$

$$\begin{aligned} \langle F_l | V | f_l \rangle = & \lambda 2^{l+\frac{1}{2}} k^{l+\frac{1}{2}} \exp\left(\frac{\pi\gamma}{2k}\right) |\Gamma(l+1-i\frac{\gamma}{k})| \\ & \times [(b_l+c)^2 + k^2]^{-l-1} \exp\left\{\frac{-2\gamma}{k} \arctan\left[\frac{k}{(b_l+c)}\right]\right\} \end{aligned} \quad (\text{C.2})$$

$$\begin{aligned} \langle F_l | V G_l V | F_l \rangle = & \lambda^2 4^{l+1} X^{2l+1} (X+b_l+c)^{-4l-4} \frac{(2l+1)!}{(-\tau+l+1)} \\ & \times {}_2F_1\left[2l+2, -\tau+l+1; -\tau+l+2; \left(\frac{X-b_l-c}{X+b_l+c}\right)^2\right] \end{aligned} \quad (\text{C.3})$$

These matrix elements are used to calculate

$$C = \frac{\langle F_l | V | f_l \rangle}{\langle F_l | V - V G_l^{(P)} V | F_l \rangle} \quad (\text{C.4})$$

and

$$\begin{aligned}\cot \delta_l &= \frac{\langle F_l | V - VG_l^{(P)} V | F_l \rangle}{|\langle F_l | V | f_l \rangle|^2} \\ &= \frac{1}{C \langle f_l | V | F_l \rangle}\end{aligned}\quad (\text{C.5})$$

which are part of the continuum wave function.

The limits $X \rightarrow 0$ of the quantities are used to affect the variational optimization of $\cot \delta_l$ at threshold. These limits are:

$$\lim_{X \rightarrow 0} \langle F_l | V | F_l \rangle = \frac{\lambda(2l+1)!}{(2b_l+1)^{2l+2}} \quad (\text{C.6})$$

$$\lim_{X \rightarrow 0} \langle F_l | V | f_l \rangle = \lambda \sqrt{\pi} 2^{l+1} (b_l + c)^{-2l-2} \exp\left(-\frac{2}{b_l + c}\right) \quad (\text{C.7})$$

$$\begin{aligned}\lim_{X \rightarrow 0} \langle F_l | VG_l V | F_l \rangle &= -\lambda^2 4^{l+1} X^{2l+1} (b_l + c)^{-4l-4} \exp\left[-\frac{2}{b_l + c}\right] \\ &\times \left\{ Ei\left(\frac{4}{b_l + c}\right) - \frac{b_l + c}{4} \exp\left(\frac{4}{b_l + c}\right) \sum_{j=0}^{2l} \left(\frac{b_l + c}{4}\right)^j j! \right\}\end{aligned} \quad (\text{C.8})$$

The normalization constant of the bound state is given by:

$$\begin{aligned}N &= \langle F_l | VG_l G_l V | F_l \rangle \\ &= \lambda \left\{ \frac{2^{2l+1} X^{2l-1}}{(X + b + c)^{4l+4}} \sum_{j=0}^{\infty} \frac{(2l+2+j)! D^{2j}}{j!} \right. \\ &\quad \left. \times \left[\frac{1}{(-\tau + l + 1 + j)} + \frac{D}{(-\tau + l + 2 + j)} \right]^2 \right\}^{\frac{1}{2}}.\end{aligned} \quad (\text{C.9})$$

The limit of N at threshold is derived from a more general way to express the normalization constant given in Ref. [33]

$$N = \sqrt{\frac{\partial}{\partial \varepsilon} \langle F_l | VG_l V | F_l \rangle}. \quad (\text{C.10})$$

The evaluated limit at $X = 0$ is

$$\lim_{X \rightarrow 0^-} N = \frac{\lambda(2\gamma)^{l+1} \exp\left(-\frac{2\gamma}{b+c}\right) \pi \tau^{3/2}}{(b+c)^{2l+2} \sin(\pi\mu)} \quad (\text{C.11})$$

Appendix D

Evaluation of R

This appendix will describe the evaluation of the terms of the radial dipole matrix element.

D.0.1 Evaluation of R for bound-continuum transitions

From Chapter 2 section 2.3 we must evaluate the following expression for a bound-continuum transition:

$$\begin{aligned} R_{\epsilon,l';n,l} &= \langle P_{\epsilon,l'} | r | P_{n,l} \rangle \\ &= \frac{-1}{\sqrt{\pi}N} \left(e^{-i\delta_{l'}} \langle f_{l'} | r \{ -G_l V | F_l \} \rangle \right. \\ &\quad \left. + \frac{\sin(\delta_{l'})}{\langle f_{l'} | V | F_{l'} \rangle} \{ \langle F_{l'} | V G_{l'}^* (+ik) \rangle r \{ G_l V | F_l \} \} \right) \\ &= \frac{-1}{\sqrt{\pi}N} \left(e^{-i\delta_{l'}} R^c + \frac{\sin(\delta_{l'})}{\langle f_{l'} | V | F_{l'} \rangle} R^s \right) \end{aligned} \quad (\text{D.1})$$

The following sections will describe the evaluation of R^c and R^s .

R^c

R^c is the term of the radial dipole matrix element for a bound-continuum transition that contains the Coulombic term of the final continuum state

$$\begin{aligned}
R^c &= \langle f_{l'} | r G_l V | F_l \rangle \\
&= \lambda \frac{2^{2l+l'+2+\frac{1}{2}}}{\Gamma(2l'+2)} X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\
&\quad \times k^{l'+\frac{1}{2}} \exp\left(\frac{\pi\gamma}{2k}\right) |\Gamma(l'+1+i\frac{\gamma}{k})| \int_c dw w^{-\tau+l} (D_l w + 1)^{-2l-2} \\
&\quad \times \int_0^\infty dr r^{l+l'+3} \exp\left[-\left(-X \frac{(D_l w - 1)}{(D_l w + 1)} - ik\right) r\right] \\
&\quad \times {}_1F_1\left(l'+1-i\frac{\gamma}{k}, 2l'+2, -2ikr\right)
\end{aligned} \tag{D.2}$$

The $\int dr$ can be evaluated directly using Eq. 7.621(4) of Ref. [38] provided that

$$\Re\left\{-X \frac{(D_l w - 1)}{(D_l w + 1)} - ik\right\} . \tag{D.3}$$

This is easily accomplished as long as $|w| < 1$, *i.e.* the contour of the w -integral must stay inside the unit circle.

Thus after the evaluation of the w -integral everything from $\int dw$ on becomes

$$\begin{aligned}
\int_c dw(\dots) &\Rightarrow \Gamma(l+l'+4) \\
&\quad \times \int_c dw w^{-\tau+l} (D_l w + 1)^{-2l-2} \left[-X \frac{(D_l w - 1)}{(D_l w + 1)} - ik\right]^{-l-l'-4} \\
&\quad \times {}_2F_1\left(l'+1-i\frac{\gamma}{k}, l+l'+4; 2l'+2; \frac{2ik}{\left[X \frac{(D_l w - 1)}{(D_l w + 1)} + ik\right]}\right)
\end{aligned} \tag{D.4}$$

This gives a form of R^c that is one possible starting point for numerical work;

$$\begin{aligned}
R^c &= \lambda \frac{2^{2l+l'+2+\frac{1}{2}}}{\Gamma(2l'+2)} \Gamma(l+l'+4) X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\
&\quad \times k^{l'+\frac{1}{2}} \exp\left(\frac{\pi\gamma}{2k}\right) |\Gamma(l'+1+i\frac{\gamma}{k})|
\end{aligned}$$

$$\begin{aligned}
& \times \int_c dw w^{-\tau+l} (D_l w + 1)^{-2l-2} \left[-X \frac{(D_l w - 1)}{(D_l w + 1)} - ik \right]^{-l-l'-4} \\
& \times {}_2F_1 \left(l' + 1 - i\frac{\gamma}{k}, l + l' + 4; 2l' + 2; \frac{2ik}{\left[X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \right]} \right) \quad (D.5)
\end{aligned}$$

The ${}_2F_1$ in the above equation can be written as a polynomial which provides another form of the R^c expression. To do this, first rewrite the ${}_2F_1$ using Eq. 15.3.3 of Ref. [44] giving:

$$\begin{aligned}
{}_2F_1 & \rightarrow \left\{ 1 - \frac{2ik}{\left[X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \right]} \right\}^{-l-3-i\frac{\gamma}{k}} \\
& \times {}_2F_1 \left(l' + 1 + i\frac{\gamma}{k}, l' - l - 2; 2l' + 2; \frac{2ik}{\left[X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \right]} \right) \quad (D.6)
\end{aligned}$$

Now the ${}_2F_1$ is in a form where parameter $\beta = l' - l - 2$ is a negative integer ($l' = l + 1 \Rightarrow \beta = -1$; $l' = l - 1 \Rightarrow \beta = -3$), so the ${}_2F_1$ becomes a terminating polynomial of order $l' - l + 2$ [see Eq. 15.1.1 of Ref. [44]. When this form is put into R^c , the result is

$$\begin{aligned}
R^c &= \lambda(-1)^{-l-l'-2} \frac{2^{2l+l'+2+\frac{1}{2}}}{\Gamma(2l'+2)} \Gamma(l+l'+4) \\
& \times X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2 \sin(\pi\tau)} \right) \\
& \times k^{l'+\frac{1}{2}} \exp\left(\frac{\pi\gamma}{2k}\right) |\Gamma(l' + 1 + i\frac{\gamma}{k})| \\
& \times \sum_{j=0}^{l-l'+2} \frac{(l' + 1 + i\frac{\gamma}{k})_j (l' - l - 2)_j}{(2l' + 2)_j j!} \left(\frac{2ik}{-1} \right)^j \\
& \times \int_c dw w^{-\tau+l} (1 + D_l w)^{l'-l+2+j} [(X - ik) - (X + ik)D_l w]^{-l'-1-i\frac{\gamma}{k}-j} \\
& \times [(X + ik) - (X - ik)D_l w]^{-l-3+i\frac{\gamma}{k}}. \quad (D.7)
\end{aligned}$$

Some might prefer to evaluate Eq. (D.7), but I chose to evaluate Eq. (D.5) because of the exceptionally accurate and stable ${}_2F_1$ routines in MathematicaTM.

R^s

In this section R^s will be evaluated.

$$\begin{aligned}
R^s &= \langle F_l | V G_l^* (+ik) r G_l V | F_l \rangle \\
&= \lambda^2 4^{l'+l+2} X^{2l+1} (X + b_l + c)^{-2l-2} \left(\frac{ie^{i\pi\tau}}{2 \sin(\pi\tau)} \right) \left(\frac{-ie^{\pi\frac{\gamma}{k}}}{2 \sin\left(\pi\frac{\gamma}{(-ik)}\right)} \right) \\
&\quad \times (ik)^{2l'+1} (ik + \tilde{b}_{l'} + c)^{-2l'-2} \\
&\quad \times \int_0^\infty dr r^{l+l'+3} \int_c dw w^{-\tau+l} (D_l w + 1)^{-2l-2} \exp \left[X r \frac{(D_l w - 1)}{(D_l w + 1)} \right] \\
&\quad \times \int_{c^*} d\rho \rho^{\gamma/(ik)+l'} (\tilde{\mathcal{D}}_{l'}^* \rho + 1)^{-2l'-2} \exp \left[-ikr \frac{(\tilde{\mathcal{D}}_{l'}^* \rho - 1)}{(\tilde{\mathcal{D}}_{l'}^* \rho + 1)} \right] \quad (D.8)
\end{aligned}$$

Sifting out all factors involving r yields

$$\begin{aligned}
&\int_0^\infty dr r^{l+l'+3} \exp \left\{ - \left[-X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \frac{(\tilde{\mathcal{D}}_{l'}^* \rho - 1)}{(\tilde{\mathcal{D}}_{l'}^* \rho + 1)} \right] r \right\} = \\
&\quad (l + l' + 3)! \left[-X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \frac{(\tilde{\mathcal{D}}_{l'}^* \rho - 1)}{(\tilde{\mathcal{D}}_{l'}^* \rho + 1)} \right]^{-l-l'-4} \quad (D.9)
\end{aligned}$$

which was evaluated using Eq. 3.381(4) of Ref [38]. For the above integral to converge we require

$$\Re \left\{ -X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \frac{(\tilde{\mathcal{D}}_{l'}^* \rho - 1)}{(\tilde{\mathcal{D}}_{l'}^* \rho + 1)} \right\} > 0.$$

Which leads to:

$$|w|^2 < 1$$

and

$$2k(\tilde{b}_{l'} + c)\Re\{\rho\} + [(\tilde{b}_{l'} + c)^2 - k^2]\Im\{\rho\} > 0 \quad (D.10)$$

These conditions are satisfied by keeping w inside the unit circle, and $\Im\{\rho\} \approx 0$ and $\Re\{\rho\} \geq 0$.

Now reorganize the factor in square brackets on the right to group things according to ρ such that

$$\left[-X \frac{(D_l w - 1)}{(D_l w + 1)} + ik \frac{(\tilde{\mathcal{D}}_{l'}^* \rho - 1)}{(\tilde{\mathcal{D}}_{l'}^* \rho + 1)} \right] = (-1) \frac{\mathcal{M}(w)\rho + \mathcal{N}(w)}{(\tilde{\mathcal{D}}_{l'}^* \rho + 1)(D_l w + 1)} \quad (\text{D.11})$$

where:

$$\mathcal{M}(w) = \tilde{\mathcal{D}}_{l'}^* [D_l \mathcal{E}_- w - \mathcal{E}_+]$$

$$\mathcal{N}(w) = D_l \mathcal{E}_+ w - \mathcal{E}_-$$

$$\mathcal{E}_+ = X + ik$$

$$\mathcal{E}_- = X - ik$$

Now gathering all terms involving ρ yields

$$\left[\frac{(D_l w + 1)}{\mathcal{N}(w)} \right]^{+l+l'+4} \int_{c^*} d\rho \rho^{\frac{\gamma}{(ik)}+l'} (\tilde{\mathcal{D}}_{l'}^* \rho + 1)^{l-l'+2} \left[1 + \frac{\mathcal{M}(w)}{\mathcal{N}(w)} \rho \right]^{-l-l'-4} \quad (\text{D.12})$$

Note that the exponent of the $(\tilde{\mathcal{D}}_{l'}^* \rho + 1)$ factor is a small positive integer ($l' = l + 1 \Rightarrow 1 : l' = l - 1 \Rightarrow 3$) so we can effectively use the binomial expansion

$$(\tilde{\mathcal{D}}_{l'}^* \rho + 1)^{l-l'+2} = \sum_{j=0}^{l-l'+2} \binom{l-l'+2}{j} (\tilde{\mathcal{D}}_{l'}^* \rho)^j. \quad (\text{D.13})$$

Now the $\int d\rho$ can be written in the form

$$\begin{aligned} (-1)^{-\frac{\gamma}{(ik)}-l'} & \left[\frac{(D_l w + 1)}{\mathcal{N}(w)} \right]^{l+l'+4} \sum_{j=0}^{l-l'+2} \binom{l-l'+2}{j} \left(\frac{\tilde{\mathcal{D}}_{l'}^*}{-1} \right)^j \\ & \times \int_{c^*} d\rho (-\rho)^{\frac{\gamma}{(ik)}+l'+j} \left[1 + \frac{\mathcal{M}(w)}{\mathcal{N}(w)} \rho \right]^{-l-l'-4}. \end{aligned} \quad (\text{D.14})$$

Here the new $\int d\rho$ is in the form of an ${}_2F_1$ given Eq. (e.3) of Ref. [48]

$$\begin{aligned} \int_{c^*} d\rho & \rightarrow \frac{(+2\pi i) \Gamma(1)}{\Gamma\left[1 - \left(\frac{\gamma}{(ik)} + l' + j + 1\right)\right] \Gamma\left[1 + \left(\frac{\gamma}{(ik)} + l' + j + 1\right)\right]} \\ & \times {}_2F_1\left(\frac{\gamma}{(ik)} + l' + j + 1, l + l' + 4; \frac{\gamma}{(ik)} + l' + j + 2; -\frac{\mathcal{M}(w)}{\mathcal{N}(w)}\right) \end{aligned} \quad (\text{D.15})$$

Next the gamma functions in the above can be written in another form using Eq. 6.1.17 of Ref. [44]

$$\frac{1}{\Gamma\left[1 - \left(\frac{\gamma}{ik}\right) + l' + j + 1\right]} \frac{1}{\Gamma\left[1 + \left(\frac{\gamma}{ik}\right) + l' + j + 1\right]} = \frac{\sin\left[\pi\left(\frac{\gamma}{ik}\right) + l' + j + 1\right]}{\left(\frac{\gamma}{ik}\right) + l' + j + 1} \pi \quad (D.16)$$

The sine function can be written as

$$\sin\left[\pi\left(\frac{\gamma}{ik}\right) + l' + j + 1\right] = \sin\left(\pi\frac{\gamma}{ik}\right) \cos[\pi(l' + j + 1)] + \cos\left(\pi\frac{\gamma}{ik}\right) \sin[\pi(l' + j + 1)] \quad (D.17)$$

And since $(l' + j + 1)$ is an integer the $\sin[\pi(l' + j + 1)] = 0$ and $\cos[\pi(l' + j + 1)] = (-1)^{l'+j+1}$. Thus

$$\frac{1}{\Gamma\left[1 - \left(\frac{\gamma}{ik}\right) + l' + j + 1\right]} \frac{1}{\Gamma\left[1 + \left(\frac{\gamma}{ik}\right) + l' + j + 1\right]} = \frac{(-1)^{l'+j+2} \sin\left[\pi\frac{\gamma}{ik}\right]}{\left(\frac{\gamma}{ik}\right) + l' + j + 1} \pi \quad (D.18)$$

Now combining all of the above and the fact that $(-1)^{\frac{\gamma}{ik}} = e^{i\pi\frac{\gamma}{ik}}$ gives the following net result for R^s

$$\begin{aligned} R^s &= (-1)^{-l-l'-3} \lambda^2 4^{l'+l+2} (l' + l + 3)! X^{2l+1} (X + b_l + c)^{-2l-2} \\ &\quad \times (-ik)^{2l'+1} (-ik + \tilde{b}_{l'} + c)^{-2l'-2} \left(\frac{ie^{i\pi\tau}}{2\sin(\pi\tau)} \right) \\ &\quad \times \sum_{j=0}^{l-l'+2} \binom{l-l'+2}{j} \frac{(\tilde{\mathcal{D}}_{l'}^*)^j}{\left(\frac{\gamma}{ik}\right) + l' + j + 1} \int_c dw w^{-\tau+l} \frac{(D_l w + 1)^{-2l-2}}{[\mathcal{N}(w)]^{l+l'+4}} \\ &\quad \times {}_2F_1\left(\frac{\gamma}{ik} + l' + j + 1, l + l' + 4; \frac{\gamma}{ik} + l' + j + 2; -\frac{\mathcal{M}(w)}{\mathcal{N}(w)}\right) \quad (D.19) \end{aligned}$$

where:

$$\mathcal{M}(w) = \tilde{\mathcal{D}}_{l'}^* [D_l \mathcal{E}_- w - \mathcal{E}_+]$$

$$\mathcal{N}(w) = D_i \mathcal{E}_+ w - \mathcal{E}_-$$

$$\mathcal{E}_+ = X + ik$$

$$\mathcal{E}_- = X - ik$$

this is the beginning for computational work.

D.0.2 Evaluation of R for bound-bound transitions

For bound-bound transitions the R matrix has only one term,

$$R_{n',l';n,l} = \frac{1}{N_{n',l'} N_{n,l}} \{ \langle F_{l'} | V G_{l'} \rangle r \{ G_l V | F_l \} \} . \quad (\text{D.20})$$

In this case the evaluation is identical to the evaluation of R^s above except that ik is replaced with $\tilde{X}$, so that

$$\begin{aligned} R_{n',l';n,l} &= \frac{1}{N_{n',l'} N_{n,l}} (-\lambda^2) 4^{l'+l+2} (l' + l + 3)! X^{2l+1} (X + b_l + c)^{-2l-2} \\ &\quad \times (\tilde{X})^{2l'+1} (\tilde{X} + \tilde{b}_{l'} + c)^{-2l'-2} \left(\frac{ie^{i\pi\tilde{\tau}}}{2 \sin(\pi\tilde{\tau})} \right) \\ &\quad \times \sum_{j=0}^{l'-l+2} \binom{l'-l+2}{j} \frac{D_l^j}{(-\tau + l + j + 1)} \int_c d\rho \rho^{-\tilde{\tau}+l'} \frac{(1 + \tilde{D}_{l'} \rho)^{l-l'+2}}{[N(\rho)]^{l'+l+4}} \\ &\quad \times {}_2F_1 \left(-\tau + l + j + 1, l + l' + 4; -\tau + l + j + 2; \frac{M(\rho)}{N(\rho)} \right) \quad (\text{D.21}) \end{aligned}$$

where:

$$M(\rho) = D_l [E_- + \tilde{D}_{l'} E_+ \rho]$$

$$N(\rho) = E_+ + \tilde{D}_{l'} E_- \rho$$

$$E_+ = X + \tilde{X}$$

$$E_- = X - \tilde{X}$$

$$\tilde{X} = \frac{\gamma}{(n' + \mu')}$$

$$\tilde{\tau} = \frac{\gamma}{\tilde{X}}$$

Vita

Ivan Cordrey was born in Fullerton, California on March 5, 1965. Educated in the Orange Unified School District of Southern California, he graduated from Canyon High School in Anaheim, California in June, 1983. Pursuing an interest in science, he began studies in chemistry at California State University, Fullerton the following September . Facinated by quantum mechanics, Mr. Cordrey changed his major to physics in 1984, but maintained an interest in chemistry. In 1988 he graduated with a Bachelor of Science in Physics with a minor in Chemistry. He relocated to Tennessee to persue graduate studies in physics at the University of Tennessee, Knoxville in August, 1988. Working first in the theory of ion-atom collisions, he published a paper on post-collision interaction. He then changed concentrations to photon-atom interactions to persue research toward his dissertation. Ivan Cordrey earned his Doctor of Philosophy in Physics in May, 1997.