Ph.D. Thesis of Jeffrey J. Kay
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Part 1

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(Thesis Supervisor)  
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Rydberg Series of Calcium Monofluoride: Spectrum, Structure, and Dynamics

by

Jeffrey J. Kay

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Abstract

This thesis summarizes progress toward the ultimate goal of building a complete structural and dynamical model for the CaF molecule. The quantum defects of the Rydberg series of the molecule, as well as their dependences on the internuclear distance and the collision energy of the outer electron, are determined through a quantum defect theory fit of an extensive data set that contains almost all of the electronic states of the molecule that have been observed to date. The result is a global representation of all possible one-electron scattering processes in approximately 90 quantum defect parameters. The utility of such a representation is then demonstrated; the equilibrium quantum defects are used to explore the interaction between electronic and rotational motions in diatomic molecules, and several interesting phenomena are uncovered which would be difficult or impossible to ascertain from a spectrum alone. Nearly all aspects of the interaction between electronic and rotational motion can in fact be understood in classical terms. The thesis concludes with a discussion of ongoing work toward understanding the physical origins of the quantum defects and their dependences on molecular geometry and the electron collision energy.

Thesis Supervisor: Robert W. Field
Title: Haslam and Dewey Professor of Chemistry
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\(^1\) One estimate places the number of emails exchanged at 2042; however, this number should be regarded as a lower bound.
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Whose names both begin with “T”!
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Chapter 1

Introduction

Understanding how energy flows within molecules is central to understanding almost all chemical phenomena. However, characterizing the pathways along which energy can be transferred is often difficult, especially when the molecule is large or highly excited. The number of possible pathways that energy can take in the redistribution process grows very quickly with the number of available modes of excitation, and new energy transfer pathways become available as the total internal energy of the molecule increases. Even in relatively simple diatomic molecules, these pathways are numerous and often severely interlinked, and are still not fully understood at the quantum state level. The intricate combinations of motions that a highly energized molecule can execute during the course of the redistribution process are often not understood at the level of simple intuition, either. In short, one would ideally like to know what to expect, how to predict it, and why things happen as they do.

The work presented in this thesis constitutes an attempt to resolve this issue by creating a unified picture of all of the things that a diatomic molecule can do, or at the very least a model which can be used to demonstrate each of them. This is not an easy task, and it is only reasonable to attempt such a feat by starting with a molecule that is already fairly well-studied. There are only three molecules which have been characterized to this extent, and therefore constitute realistic choices: $\text{H}_2$, $\text{H}_2^+$,
NO, and CaF. Naturally, CaF is our molecule of choice, as nearly all of its electronic states are Rydberg states, these Rydberg states are accessible using standard spectroscopic techniques, and because its ionic structure lends itself most readily to simple, intuitive electronic structure models.

This thesis is divided into a number of parts, each of which represents one portion of the composite image that is molecular structure and dynamics. These parts are arranged as follows:

- **Chapter 2** presents a review of the necessary theoretical underpinnings, and **Chapter 3** presents an in-depth look at quantum defect theory and many of its potential applications. Quantum defect theory forms, in many ways, the heart of this thesis, as it allows so many seemingly disparate phenomena to be described concisely and uniformly.

- **Chapter 4** gives a description of the spectra from which data are harvested, the techniques used to record them, and the tools used to rigorously assign them. **Chapter 5** describes how these data are input to the global quantum defect model, and the procedure by which they are fit. The resulting set of quantum defects and their derivatives with respect to molecular geometry and the electron collision energy allows almost the entire electronic spectrum to be represented in ~80 parameters.

- **Chapter 6**, Dynamics, shows the great utility of this type of global model and how it can be used to forecast new phenomena.
Chapter 7, Mechanism, presents the results of current work which aims to develop an understanding of the origins of the quantum defects, the quantities which allow this global representation in the first place, in terms of simpler and more physically-intuitive theories.

Much of the theory used to describe Rydberg states is concentrated in the first few chapters, although a fair amount is to be found in the later chapters as well. Chapters 4, 5, 6, and 7 are composed primarily of original research results. For easy reference, a list of quantum numbers and symbols used throughout the thesis can be found on the next page.
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<thead>
<tr>
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<th>Definition</th>
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<tbody>
<tr>
<td>( n )</td>
<td>Principal quantum number</td>
</tr>
<tr>
<td>( n^* )</td>
<td>Effective principal quantum number</td>
</tr>
<tr>
<td>( \ell )</td>
<td>Orbital Angular Momentum of the Rydberg Electron</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Projection of the orbital angular momentum along the internuclear axis (axis of quantization in case (b))</td>
</tr>
<tr>
<td>( \ell_R ) or ( \ell_{N^*} )</td>
<td>Projection of the orbital angular momentum along the rotation axis (axis of quantization in case (d))</td>
</tr>
<tr>
<td>( N^* )</td>
<td>Total angular momentum of the Ion core, neglecting spin</td>
</tr>
<tr>
<td>( R )</td>
<td>Rotational angular momentum of the molecule (( R = N^* ) for a ( ^1\Sigma^+ ) ion core)</td>
</tr>
<tr>
<td>( N )</td>
<td>Total angular momentum of the molecule, neglecting spin</td>
</tr>
<tr>
<td>( J )</td>
<td>Total angular momentum of the molecule; ( J = R+L+S )</td>
</tr>
<tr>
<td>( p )</td>
<td>Parity (( p=0 ) for positive parity; ( p=1 ) for negative parity)</td>
</tr>
<tr>
<td>( (\pm) )</td>
<td>Kronig symmetry; symmetry of electronic wavefunction under reflection through a plane containing the nuclei (i.e. ( \sigma_v ) symmetry). Written “(+)” if invariant to reflection; “(−)” if wavefunction changes sign upon reflection.</td>
</tr>
<tr>
<td>( \mu_{\ell\ell'}^{(\lambda)} )</td>
<td>An element of the short-range quantum defect matrix</td>
</tr>
<tr>
<td>( K_{\ell\ell'}^{(\lambda)} )</td>
<td>An element of the short-range reaction matrix</td>
</tr>
<tr>
<td>( K_{NN^*V^<em>V'^</em>} )</td>
<td>An element of the long-range reaction matrix</td>
</tr>
<tr>
<td>( \mu_\alpha ) or ( \mu_\alpha^{(\lambda)} )</td>
<td>Eigenquantum defect</td>
</tr>
<tr>
<td>( E )</td>
<td>Total energy, referenced to the ( N = 0, v = 0 ) level of the ground electronic state of the neutral molecule</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Binding energy of the Rydberg electron</td>
</tr>
</tbody>
</table>
Chapter 2

Basic Theory

This chapter presents the basic theoretical concepts that underpin the remainder of this thesis. Since molecular electronic structure is most often treated in terms of the Born-Oppenheimer approximation, this is discussed first. Nonadiabatic interactions, which invalidate the Born-Oppenheimer approximation and give rise to energy exchange between electronic and nuclear degrees of freedom, are discussed next. The different classes of Rydberg states are then introduced, and the types of nonadiabatic interactions they experience are emphasized.

2.1 The Born-Oppenheimer Approximation

The flow of energy in isolated molecules is typically understood in the framework of the Born-Oppenheimer approximation [1]. In the Born-Oppenheimer approximation the molecular Hamiltonian is first divided into electronic and nuclear terms,

\[ H = T^e(r) + V(r, R) + T^N(R, \theta, \phi) = H_{el}(r, R) + T^N(R, \theta, \phi). \]  \hspace{1cm} (2.1)

In Eq. (2.1), \( T^e(r) \) is the electron kinetic energy operator, \( V(r, R) \) consists of the interelectron repulsion terms and electron-nuclear attraction terms, \( T^N(R, \theta, \phi) \) is the nuclear kinetic energy operator, and \( H_{el}(r, R) \) is the
The molecular wavefunctions are then expressed as Born-Oppenheimer products of electronic and nuclear wavefunctions:

$$\Psi = \phi (r; R) \chi_{v}(R, \theta, \phi),$$  \hspace{1cm} (2.2)

and the solution of the electronic Schrödinger equation

$$H_{el} (r; R) \phi (r; R) = E_{el} \phi (r; R)$$  \hspace{1cm} (2.3)

gives a set of adiabatic potential energy potential energy curves which govern the motion of the nuclei. The nuclear kinetic energy operator $T^{N} (R, \theta, \phi)$ can be resolved further into vibrational and rotational components:

$$T^{N} (R, \theta, \phi) = -\frac{\hbar^{2}}{2\mu R^{2}} \left[ \frac{\partial}{\partial R} \left[ R^{2} \frac{\partial}{\partial R} \right] - R^{2} \right]$$

$$= -\frac{\hbar^{2}}{2\mu} \left[ \frac{\partial^{2}}{\partial R^{2}} + \frac{2}{R} \frac{\partial}{\partial R} \right] + \frac{\hbar^{2}}{2\mu R^{2}} R^{2}.$$  \hspace{1cm} (2.4)

$$= H_{vib} (R) + H_{rot} (R, \theta, \phi)$$

Here, $\mu$ represents the reduced mass of the system, and $R$ represents the rotational angular momentum. The nuclear wavefunctions $\chi_{v}(R, \theta, \phi)$ are then found by solving the nuclear Schrödinger equation

$$\left[ T^{N} (R, \theta, \phi) + E_{el} \right] \chi_{v}(R, \theta, \phi) = E_{tot} \chi_{v}(R, \theta, \phi),$$  \hspace{1cm} (2.5)

and the total energy of the molecule is thus expressed as

$$E_{tot} = E_{el} + E_{vib} + E_{rot},$$  \hspace{1cm} (2.6)

which reflects the partitioning of the Hamiltonian into electronic, vibrational, and rotational parts.
2.2 Nonadiabatic Interactions

At low energy, there is little or no interaction between the electronic and nuclear degrees of freedom, and the nuclear motion is usually confined to one potential energy curve. As the energy increases, however, nonradiative transitions between these curves are possible. These are termed “nonadiabatic” transitions and are due to the neglect of the effects of the nuclear kinetic energy operator $T^N(R, \theta, \phi)$ on the Born-Oppenheimer wavefunctions [1-3]. Vibrationally nonadiabatic interactions (or “vibronic” interactions) caused by the vibrational Hamiltonian,

$$\hat{H}_{\text{vib}} = -\frac{\hbar^2}{2\mu} \left[ \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right],$$  \hspace{1cm} (2.7)

couple the electronic and vibrational degrees of freedom, and result in electronic—vibrational energy exchange. Rotationally nonadiabatic interactions caused by the neglect of parts of the rotational Hamiltonian, and especially in our case the off-diagonal portion of $\hat{H}_{ro}$ known as the “$\ell$-uncoupling” operator [1],

$$\hat{H}_{\text{ro}}^{(1)} = -B(R) \left[ N^+ \ell^- + N^- \ell^+ \right],$$  \hspace{1cm} (2.8)

couple the electronic and rotational degrees of freedom, and result in electronic—rotational energy exchange. We will see evidence of these two types of interactions repeatedly throughout this work.

Rydberg states are in many ways a case study in nonadiabatic interactions. As one ascends a Rydberg series, the classical frequency of electronic motion becomes progressively slower, and eventually becomes so slow that electronic motion occurs on the timescale of the vibrational (and even rotational) motion of the molecule. Energy exchange between the
Rydberg electron and ion core then becomes both rapid and efficient. Quantum-mechanically, this means that the energy level patterns become extensively perturbed and that irregularity in the energy level positions becomes the rule rather than its exception.

Naturally, as the nonadiabatic interactions become more prominent in the energy level patterns, they become more difficult to account for concisely in a theoretical model. At low energy, nonadiabatic effects are usually weak and can be accounted for perturbatively in a standard Hamiltonian formalism [4-5]. At higher energies, the increased number of interacting states makes such a procedure prohibitive, and it becomes necessary to seek an alternate strategy. Quantum defect theory [6-9], which is described in Chapter 3, fills this need perfectly.

### 2.3 Rydberg States and Quantum Defects

The simplest zero-order picture of a Rydberg state, in atoms and molecules alike, is that of a free atomic or molecular ion with a loosely-bound electron residing in its long-range Coulomb field. The typical partitioning [6-10] of the Hamiltonian into Coulomb, ion core, and interaction terms,

\[ \hat{H} = \hat{H}_{\text{Coulomb}} + \hat{H}_{\text{Core}} + \hat{H}_{\text{nl}}^{(l)}, \]  

(2.9)

reflects this physical picture. The operator \( \hat{H}_{\text{nl}}^{(l)} \) represents all interactions between the electron and ion except the long-range Coulomb interaction; in the most general sense, this consists of repulsion between the Rydberg electron and all core electrons, as well as attraction between the Rydberg electron and all nuclei. Because the interaction term \( \hat{H}_{\text{nl}}^{(l)} \) can usually be treated as a perturbation, the energy levels of any Rydberg series, atomic or
molecular, bear a strong resemblance to those of the hydrogen atom and invariably conform to some variation on the Rydberg formula,

\[ E_n = E_{\text{ion}} - \frac{\mathcal{R}}{n^2}, \]  

(2.10)

at least in zero-order.

The Rydberg formula (2.10) is typically modified to reproduce the observed energy levels by allowing the principal quantum number to become noninteger,

\[ E_n = E_{\text{ion}} - \frac{\mathcal{R}}{n^{*2}}, \]  

(2.11)

where \( n^* = n - \mu \) is the “effective principal quantum number”, and the difference from integer is \( \mu \), the “quantum defect”. The form of the quantum defect, and the explicit form of the modified Rydberg equation used to represent the energy levels, depends on the complexity of the system in question. This is illustrated in Figure 2-1. In the hydrogen atom, the quantum defect is exactly zero, and thus each Rydberg series conforms exactly to the Rydberg equation (2.10). The core of alkali atoms carries a much higher nuclear charge than a single proton, and although the core electrons shield the Rydberg electron from the nucleus to some extent, this shielding is of course incomplete and the degree of shielding depends on \( \ell \). The Rydberg series of alkali atoms are therefore characterized by positive quantum defects that depend strongly on the orbital angular momentum of the Rydberg electron and also slightly on its collision energy \( \varepsilon \):

\[ E_{n\ell} = E_{\text{ion}} - \frac{\mathcal{R}}{\left(n - \mu(\ell, \varepsilon)\right)^2}. \]  

(2.12)

This is illustrated in Figure 2-2.
Figure 2-1: Illustration of the building-up of quantum defects in atoms and molecules.

\[ E_n = -\frac{\mathcal{R}}{n^2} \quad E_{n\ell} = -\frac{\mathcal{R}}{(n-\mu_\ell)^2} \quad E_{n'\ell'A} = -\frac{\mathcal{R}}{(n-\mu_\ell^{(A)}(R))^2} \]

Figure 2-2: Differences between the energy level patterns in atomic hydrogen and an alkali atom. The energy levels of the alkali atom are depressed relative to those of the hydrogen atom because of the increased effective nuclear charge felt by the Rydberg electron while it is inside the core.
The Rydberg series of molecules carry additional complexity beyond that of the multielectron atom. First, the quantum defects generally depend on the geometry of the molecule, since the shape of the core charge distribution changes as bonds are stretched or bent. In diatomic molecules, for example, the quantum defects are functions of both the internuclear distance $R$ and the electron binding energy $\varepsilon$ [11-13]; i.e. $\mu(R,\varepsilon)$. The lack of spherical symmetry in molecules also gives rise to strong inhomogeneous electric fields which mix the electron orbital angular momentum $\ell$, and the one-dimensional quantum defect of alkali atoms becomes a nondiagonal quantum defect matrix.

There are also at least two zero-order pictures in which molecular Rydberg states can be described. At low principal quantum numbers, where the motion of the Rydberg electron is always fast compared to the nuclei, the energy level structure is governed by the “eigen-quantum defect” [6-9, 14] of the series in question, which usually written as $\mu^{(\lambda)}(R,\varepsilon)$ or $\mu^{(\lambda)}(R,\varepsilon)$:

$$E_{n',\ell',\lambda} = E_{\text{tot}} - \frac{\hbar^2}{\left(n - \mu^{(\lambda)}(R,\varepsilon)\right)^2}.$$  (2.13)

The symbols ‘$\ell$’ and $a$ are indices denoting the state’s nominal $\ell$ character, since $\ell$ is not generally a good quantum number in the molecule. At very high principal quantum numbers, when the motion of the Rydberg electron is slower than that of the nuclei, one has instead a Rydberg series converging to each rovibrational level of the ion core [15-21], as illustrated in Figure 2-3. The zero-order positions of the energy levels are determined by
Figure 2-3: Differences between the energy level patterns in an alkali atom and a molecule. At least one zero-order Rydberg series converges to each rovibronic energy level of the ion core.

![Energy Level Diagram]

A set of quantum defects which depend on the electronic, rotational, and vibrational quantum numbers of the core \((\Lambda^+, N^+, \nu^+)\):

\[
E_{n(\Lambda^+, N^+, \nu^+)} = E_{\Lambda^+, N^+, \nu^+} - \frac{\mathcal{R}}{(n - \mu_{\Lambda^+, N^+, \nu^+})^2}.
\] (2.14)

The problem, of course, is that no Rydberg series actually conforms to any of the forms of the Rydberg equation presented in Equations (2.11), (2.12), (2.13), or (2.14). While the zero-order energy levels can be expressed in forms such as these, interactions between the zero-order states always take place to some extent through \(\hat{H}_\text{el}^{(1)}\). Since these interactions are most strongly felt when zero-order levels become nearly degenerate, the energy level patterns frequently have a very irregular appearance, similar to the diagram shown in Figure 2-4. To a large extent, these apparent
irregularities in the spectrum are entirely what we wish to understand; what we wish to achieve is a more or less complete understanding of all of the effects of \( \hat{H}_\text{el}^{(1)} \).

![Diagram showing zero-order picture and observed levels](image)

**Figure 2-4:** Differences between the zero-order picture of Rydberg states and the energy level patterns that are actually observed.

## 2.4 Classes of Rydberg States

The Rydberg states of atoms and molecules are usually organized into two very distinct categories, according to the nature of the orbit of the excited electron: Rydberg states are termed “core-penetrating” when the wavefunction of the Rydberg electron has significant amplitude inside the
inner electron shells, and are termed “core-nonpenetrating” when it does not. Although only a small fraction of the probability density of the Rydberg electron wavefunction lies near the nuclei in both cases, the degree to which the electron wavefunction penetrates inside the inner electron shells has a profound impact on the properties of the state in question.

Structurally and conceptually, nonpenetrating states are generally simpler than penetrating states. Since in nonpenetrating states the outer electron does not enter the region of space occupied by the inner electron shells, its wavefunction has no overlap with that of the core electrons. Thus, one need only consider the long-range forces between the electron and ion core: the electrostatic interactions through the multipole fields of the core and the polarization of the core by the outer electron. This “long-range model” has been successfully applied to both atoms and molecules numerous times with great success [22-26].

In penetrating states, on the other hand, the wavefunction of the outer electron does overlap that of the core electrons, and consequently experiences not only the long-range interactions described above but also Coulomb and exchange interactions with the inner electrons at short range. Calculations of the properties of core-penetrating Rydberg states are therefore more complicated. However, this increased complexity is offset by a dramatic increase in richness of dynamical behavior: on account of the overlap with the core orbitals, penetrating Rydberg states can participate in important chemical processes such as dissociation and electron rearrangements, and penetrating Rydberg orbitals often display bonding- and anti-bonding behavior [27-29].
Since all effects due to electron spin will be neglected in this thesis, it is possible to distinguish three separate dynamical regimes, which are defined according to the relative timescales of electronic, vibrational, and rotational motion. Every Rydberg series will at some point pass through each regime, and its energy level patterns will change accordingly. At low \( n^* \), electronic motion is much faster than either vibrational or rotational motion. The electronic energy level spacings are accordingly much larger than the ion core vibrational or rotational energy level spacings, and the molecule rotates and vibrates more or less as one unit. At intermediate \( n^* \), electronic motion can be slower than vibration but still faster than rotation. This occurs when the electronic energy level spacings are smaller than the vibrational energy level spacings but still larger than the core rotational energy level spacings. Here, the electronic motion is “decoupled” from the vibrational motion (meaning that the ion core vibrates freely, irrespective of the behavior of the Rydberg electron) but the electronic motion still follows the rotational motion of the core. Finally, at high \( n^* \), electronic motion is the slowest of all, and this of course occurs when the electronic energy level spacings are the smallest of all three. Under these circumstances, the electronic motion is decoupled from both vibration and rotation, and the ion core and Rydberg electron execute motions independently of one another. In the first two dynamical regimes, at low- and intermediate- \( n^* \), the molecule is in what is known as the “Hund’s Case (b) limit”. At the extreme end of the third regime the system is in what is known as the “Hund’s Case (d) limit”. Hund’s cases are discussed extensively in References [30]-[32].
2.4.1 Hund’s Case (b)

In Hund’s case (b), the motion of the Rydberg electron is fast enough that it follows the motion of the nuclei, and remains coupled to the internuclear axis of the molecule through the anisotropic electrostatic interactions between the two particles. The electron's orbital angular momentum $\ell$ is therefore quantized along the internuclear axis with projection $\lambda$. Neither the orbital angular momentum of the electron $\ell$ nor the rotational angular momentum of the ion core $N^+$ are strictly conserved; the molecule “rotates as a whole” and only the total angular momentum of the molecule $N$ remains a constant of the motion. Accordingly, the pattern-forming rotational quantum number in case (b) is $N$, the total angular momentum apart from spin, and the rotational energy is $E_{rot} = BN(N+1)$. A transition from case (b) toward the opposite limit, case (d), generally takes place in the rotating molecule as the principal quantum number $n$ increases. The $\ell$-uncoupling interaction [Eq. (2.8)], which may be described as a Coriolis interaction between rotational and electronic motion, is responsible for this transition [1, 16].

Spectroscopically, Hund’s case (b) coupling is characterized by the presence of well-separated electronic states and regular rotational energy level patterns [1, 30]. Rydberg states in case (b) are referred to using the notation $n'\ell'\Lambda$ or $n^{2\ell+1}\Lambda^\pm$; i.e. $5f\Sigma$ or $5.07^2\Sigma^+$. Due to extensive $\ell$-mixing, the latter notation is typically used in CaF. State labels and nominal $\ell$ characters for the Rydberg series of CaF are given in Table 2-1.
\[
\begin{array}{ccccccc}
\Lambda & \text{Nominal } \ell & \text{Designation} & \%s & \%p & \%d & \%f \\
0 & s & n.55 \Sigma & 74 & 26 & 0 & 0 \\
0 & p & n.88 \Sigma & 25 & 71 & 3 & 1 \\
0 & d & n.19 \Sigma & 1 & 3 & 65 & 31 \\
0 & f & n.07 \Sigma & 0 & 0 & 33 & 67 \\
1 & p & n.36 \Pi & 64 & 35 & 1 & \\
1 & d & n.98 \Pi & 36 & 64 & 0 & \\
1 & f & n.07 \Pi & 0 & 2 & 98 & \\
2 & d & n.14 \Delta & & 98 & 2 & \\
2 & f & n.00 \Delta & & 2 & 98 & \\
3 & f & n.93 \Phi & & & & 100 \\
\end{array}
\]


2.4.2 Hund’s Case (d)

In Hund’s case (d) the electron and ion move more or less independently of one another and consequently the angular momenta of the individual particles, \(\ell\) and \(N^+\), are approximately conserved. The electron orbital angular momentum is quantized along the rotation axis of the molecule, with projection \(\ell_{ro}\), and the pattern-forming rotational quantum number is the rotational quantum number of the free ion \(N^+\), with rotational energy \(E_{rot} = BN^+ \left( N^+ + 1 \right) \).

Spectroscopically, the gross structure of states in the case (d) limit is actually rotational structure, with the electronic structure superimposed as fairly narrow energy level splittings [30, 33-34]. States in the case (d) limit typically appear as groups of narrowly-split rotational branches. Case (d)
Rydberg states are typically referred to using the notation $n\ell(\ell_r)^\pm$, where the $\pm$ superscript indicates Kronig symmetry [30] and $\ell_r = N - N^+$. For example, the Rydberg state with $n=10$, $\ell = 3$, $N = 5$, $N^+ = 3$ has $(-)$ Kronig symmetry and is labeled $10f(+2)^-$.  

The energy level patterns of states *intermediate* between cases (b) and (d) can be quite irregular: the transition from one coupling case to another is accompanied by unusual and abrupt changes in the rotational energy level patterns. This can make the identification of rotational branches difficult, as is discussed extensively in Chapter 4. Occasionally, nonpenetrating Rydberg states intermediate between cases (b) and (d) are referred to using their nominal case (b) quantum numbers. Table 2-2 indicates the appropriate correspondence between the case (b) labels (appropriate at low $N$) and the case (d) labels (appropriate at high $N$).
<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$\ell_R$</th>
<th>$\Lambda$</th>
<th>$\pm$</th>
<th>Case (b) Label</th>
<th>Case (d) Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-3</td>
<td>0</td>
<td>(+)</td>
<td>f(-3)$^+$</td>
<td>f$\Sigma^+$</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>1</td>
<td>(-)</td>
<td>f(-2)$^-$</td>
<td>f$\Pi^-$</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>1</td>
<td>(+)</td>
<td>f(-1)$^+$</td>
<td>f$\Pi^+$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>(-)</td>
<td>f(0)$^-$</td>
<td>f$\Delta^-$</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>2</td>
<td>(+)</td>
<td>f(+1)$^+$</td>
<td>f$\Delta^+$</td>
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<tr>
<td></td>
<td>+2</td>
<td>3</td>
<td>(-)</td>
<td>f(+2)$^-$</td>
<td>f$\Phi^-$</td>
</tr>
<tr>
<td></td>
<td>+3</td>
<td>3</td>
<td>(+)</td>
<td>f(+3)$^+$</td>
<td>f$\Phi^+$</td>
</tr>
<tr>
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<td>(-)</td>
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<td>(-)</td>
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<tr>
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<td>3</td>
<td>(+)</td>
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<td>g$\Phi^+$</td>
</tr>
<tr>
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<td>4</td>
<td>(-)</td>
<td>g(+3)$^+$</td>
<td>g$\Gamma^-$</td>
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<tr>
<td></td>
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<td>4</td>
<td>(+)</td>
<td>g(+4)$^-$</td>
<td>g$\Gamma^+$</td>
</tr>
</tbody>
</table>

Table 2-2. Quantum numbers of $f$ ($\ell = 3$) and $g$ ($\ell = 4$) Rydberg states in the case (b) and case (d) limits.
2.5 Bibliography


Chapter 3

Quantum Defect Theory

Quantum defect theory [1-4], the primary theory in use to describe the structure of molecular Rydberg states, is a compact, elegant, and generally nonperturbative way of accounting for all of the fine details observed in molecular Rydberg spectra, from strong vibronic perturbations to fragmentation and even fine spin structure. Several forms of the theory, and a number of possible extensions to them, are outlined here.

3.1 Bound States: Asymptotic Formulation

Quantum defect theory begins with the division of the molecular Hamiltonian into Rydberg electron, ion core, and interaction terms [5]:

\[ \hat{H} = \hat{H}_{\text{Coulomb}} + \hat{H}_{\text{Core}} + \hat{H}_{\text{el}}^{(1)}. \]  

(3.1)

Here, \( \hat{H}_{\text{Core}} \) represents the full Hamiltonian of the ion core, \( \hat{H}_{\text{Coulomb}} \) is the Coulomb Hamiltonian, and \( \hat{H}_{\text{el}}^{(1)} \) contains all of the interactions between the electron and each of the core particles: repulsion between the Rydberg electron and each of the core electrons and attraction between the Rydberg electron and the two nuclei. The goal of quantum defect theory is to parameterize all of the effects of \( \hat{H}_{\text{el}}^{(1)} \), ideally in as compact of a form as possible.

Probably the most commonly-used formulation of quantum defect theory is the “asymptotic” formulation [1-4]. It is so-named because the
wavefunction of the system is expressed in terms of a set of electron-ion product functions:

\[ \psi_{\ell v^+N^+} = \left[ f_{\ell v^+N^+} \delta_{v^+N^+;v^+N^+} - \sum_{\ell' v'\ell'' v''} K_{\ell v^+N^+;\ell' v'N''} g_{\ell' v'N''} \right] \chi_{v^+}^{N^+} \Phi_{\ell N^+}^{(N)}, \quad (3.2) \]

whose division into products reflects the lack of interaction between the electron and ion at long range; i.e. in the “asymptotic” region. The quantity in brackets is the radial wavefunction of the Rydberg electron, \( \Phi_{\ell N^+}^{(N)} \), represents the combined angular wavefunctions of the Rydberg electron and the ion core (coupled to form eigenfunctions of \( N^2 \)), and \( \chi_{v^+}^{N^+} \) is the vibrational wavefunction of the core (which depends slightly on the core rotational quantum number \( N^+ \)). The functions (3.2) are referred to as “channel functions”, and each possible combination of the quantum numbers of the system (in our case the four numbers \( \ell, N^+, N^-, \) and \( v^+ \)) constitutes one unique “channel”. The interaction term \( \hat{H}^{(0)}_{el} \) in Eq.(3.1), which describes the interactions between the Rydberg electron and the ion core, allows the system to pass from one channel to another. The reaction matrix \( K \), whose elements appear as coefficients of the irregular Coulomb function in Eq. (3.2), describes the probability with which transitions between channels occur and determines nearly all aspects of the energy level structure. For this reason, the asymptotic formalism is also known as the “reaction matrix” formalism. Because the system can scatter from one channel to another, the full molecular wavefunction is written as a superposition of channel functions:

\[ \Psi_{\ell v^+} = \sum_{\ell N^+ v^+} B_{\ell N^+ v^+} \psi_{\ell N^+ v^+}, \quad (3.3) \]
where the coefficients $B_{iN^+\nu'}$, called “channel mixing amplitudes”, provide a measure of the fractional amplitude of the system in each channel.

In principle, boundary conditions can be applied to the total wavefunction (3.3), which will rise to a system of equations which can be solved to locate the energy levels of the system. However, as it stands, the reaction matrix $\mathbf{K}$ is so large that it is not possible to either guess the values of its matrix elements or calculate them from first principles. In a typical calculation for a single value of $N$, one would generally allow for interactions among all possible channels with $\ell \leq 3$ and $\nu \leq 5$. $\mathbf{K}$ will then have at least 60 rows, at least 60 columns, and at least $n(n+1)=1830$ independent elements.

This problem is elegantly solved using what is known as the “frame transformation” [5, 6-7]. The idea underlying the frame transformation is that the classical frequency of motion of the Rydberg electron changes according to its distance from the core. Space is divided into three regions: one in which the electron lies within the core (region A); one in which the electron lies outside the core, but in which its motion is still fast compared to that of the nuclei (region B); and one in which the electron lies outside the core, and in which its classical motion is much slower than the motion of the nuclei (region C). This is illustrated schematically in Figure 3-1.
Figure 3-1: Division of space in quantum defect theory. Here, \( r_c \) denotes the core boundary, and \( r_{vr} \) denotes some distance at which the classical orbital motion of the Rydberg electron occurs on the same timescale as the nuclei.

When the electron is in region B, its classical orbital motion is much faster than the vibrational and rotational motion of the nuclei. Thus, in this range, the Born-Oppenheimer approximation holds, and the wavefunction of the molecule may be written accordingly:

\[
\Psi_B = \sum |el\rangle|vib\rangle|rot\rangle
\]  

(3.4)

Outside this range, in region C, the classical orbital motion of the electron is much slower than either vibration or rotation, and the motions of the two particles are completely separable. Thus, the wavefunctions are then written (rather than as a sum over Born-Oppenheimer products) as a sum over electron-ion products:

\[
\Psi_C = \sum |Ryd\rangle/ion\rangle = \sum |Ryd\rangle|el_{ion}\rangle|vib_{ion}\rangle|rot_{ion}\rangle.
\]  

(3.5)

On the hypothetical dividing surface \( r = r_{vr} \) (see Fig. 3-1), the wavefunctions must be equally, no matter how they are expressed. By equating the two forms of the wavefunction,
\[ \Psi_{r_{v_{v}}} = \sum_j A_j |e\rangle|vib\rangle|rot\rangle = \sum_j B_j |Ryd\rangle|e\rangle|vib\rangle|rot\rangle, \]

and considering their explicit forms (a procedure discussed extensively in [5]), it is possible to express the long-range reaction matrix \( K \) (which describes the passage of the system from one rovibronic channel to another) in terms of a handful of short-range quantum defects \( \mu \) (which describes the scattering of the electron from one purely electronic channel to another):

\[ K_{r_{v'}^{N'+1},v'^{N-1}} = \sum_{\Lambda} \langle \Lambda | N^+ \rangle^{(N)} \left[ \int \chi_{\nu'}^{N'}(R) \tan \pi \mu_{\ell \ell'}^{(A)}(R) \chi_{\nu}^{N}(R) dR \right] \langle N^+ | \Lambda \rangle^{(N)}. \]  

Equation (3.7) constitutes the rovibronic frame transformation, and allows the typically large number of the reaction matrix elements \( K_{v_{v'}} \) to be expressed in terms of the much smaller number of quantum defect matrix elements \( \mu_{\ell \ell'}^{(A)} \). The reduction in the number of adjustable parameters is considerable; while \( K \) typically has more than 1000 independent elements, using the rovibronic frame transformation it can be expressed in terms of approximately twenty to sixty quantum defect parameters. The rotational coefficients \( \langle \Lambda | N^+ \rangle^{(N)} \) in the frame transformation expression are purely geometric quantities, and are given in Reference [8] as:

\[ \langle \Lambda | N^+ \rangle^{(N)} = (-1)^{N-\Lambda} \left( \frac{1+(-1)^{p-\ell}}{2} \right) \left[ \frac{2}{(1+\delta_{\ell \ell'})} \right]^{\frac{1}{2}} \left( 2N^+ +1 \right)^{\frac{1}{2}} \left( \begin{array}{ccc} N+ & \ell & N \\ \Lambda & -\Lambda \end{array} \right). \]

Energy levels are found by demanding the wavefunction vanish at infinite electron ion separation. Upon consideration of the explicit forms of the Coulomb functions appearing in Eq. (3.2), this gives a homogeneous linear system of equations,

\[ \left[ P(E) + K \right] B = 0 \]

54
which can be solved numerically. Here, \( P \) is the “phase matrix” [9],

\[
P(E) = \begin{pmatrix}
\tan \pi \nu_{r,N^+} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \tan \pi \nu_{r,N^++1} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \tan \pi \nu_{r,N^++2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \tan \pi \nu_{r+1,N^+} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \tan \pi \nu_{r+1,N^++1} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \tan \pi \nu_{r+1,N^++2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots
\end{pmatrix}
\]

(3.10)

and \( K \) is the reaction matrix, whose elements are given by Eq. (3.7). The system (3.10) has a solution when the determinant of the coefficient matrix vanishes:

\[
\det [P(E) + K] = 0
\]

(3.11)

and the coefficients \( B_{l(N^+)r} \) can be found at each such energy by finding the eigenvector of the matrix \((P(E)+K)\) whose associated eigenvalue is zero.

### 3.2 Bound States: Eigenchannel Formulation

While quantum defect theory is often expressed in terms of the asymptotic formulation described in Section 3.1, which takes the division of the molecule into a noninteracting Rydberg electron and ion core subunits as its starting point, it is also possible to describe the problem in a form more analogous to the Born-Oppenheimer picture from the very beginning. In this picture, the asymptotic channel functions of Eq. (3.2) are replaced with “eigenchannel” functions [2, 6-7]:

\[
\psi_{a\Lambda r} = \psi_{a\Lambda} \chi_{sd}^{(a)} ,
\]

(3.12)
in which
\[ \psi_{\alpha \Lambda} = \sum \langle \ell | \alpha^{(\Lambda)} \left[ f_{\ell} - \tan \mu_{a}^{(\Lambda)} g_{\ell} \right] \Phi_{\ell} \].  \hfill (3.13)

Here, \( \mu_{a}^{(\Lambda)} \) are the “eigenquantum defects”, which are derived from the eigenvalues of the short-range reaction matrix through a matrix diagonalization:
\[ U^T K^{(\Lambda)} U = \tan \mu_{a}^{(\Lambda)}. \]  \hfill (3.14)

Here, \( U \) is the matrix that diagonalizes \( K \). Again, owing to couplings between the electron and ion core, the wavefunction of the system is most generally written as a superposition of channels functions:
\[ \Psi = \sum_{\alpha \Lambda} A_{\alpha \Lambda} \psi_{\alpha \Lambda} \]  \hfill (3.15)

and energy levels are found by again demanding that the wavefunctions vanish at infinite electron-ion separation. This again gives a homogeneous linear system of equations, which in this case has the form [2]
\[ \sum_{\alpha} F_{i\alpha}(E) A(E) = 0. \]  \hfill (3.16)

that can be solved to locate energy levels. The quantities in Eq. (3.16) are
\[ F_{i\alpha}(E) = C_{i\alpha} \sin \pi \nu_{i}(E) + S_{i\alpha} \cos \pi \nu_{i}(E) \]
\[ C_{i\alpha} = U_{i\alpha} \cos \pi \mu_{a} \]
\[ S_{i\alpha} = U_{i\alpha} \sin \pi \mu_{a} \]  \hfill (3.17)

The eigenchannel functions of Eq. (3.12) are related to the asymptotic channel functions of Eq. (3.2) through the matrix relationship
\[ \psi_{a} = \psi_{i} U \cos \pi \mu_{a}, \]  \hfill (3.18)

where \( U \) represents the frame transformation matrix [2].

Although the asymptotic and eigenchannel formulations of quantum defect theory give identical results, one of the two formulations is often more
convenient to use or is more representative of the physical situation at hand. The two formulations represent the two “extreme cases” of Rydberg states; the asymptotic formulation, in which the zero-order picture is that of two completely noninteracting particles, is most appropriate at very high quantum numbers where the electron is always found far from the core. That is, at very high \( n \), one of the \( B_{N',\nu'} \approx 1 \), and the expansion \( \Psi = \sum_j B_j \psi_j \) reduces to \( \Psi \approx \psi_j \). The system is then found primarily in one fragmentation channel. On the other hand, at very low \( n \) the eigenchannel picture is more appropriate, since the electron is always close to the core. Under these circumstances it is typically the case that one of the \( A_{\alpha\nu} \approx 1 \), and so the expansion \( \Psi = \sum_\alpha A_\alpha \psi_\alpha \) reduces to \( \Psi \approx \psi_\alpha \). A particular advantage of the eigenchannel formulation is that its adjustable parameters, the eigenquantum defects, can be derived directly from the potential energy curves themselves. The relationship between the eigenquantum defect of a Rydberg state and its potential energy curve is [1-5, 10]

\[
V_{n\Lambda} (R) = V_{\text{ion}} (R) - \frac{\Re}{\left( n - \mu^{(\Lambda)}_\alpha (R) \right)^2}.
\] (3.19)

This is illustrated schematically in Figure 3-2.
Figure 3-2. Schematic diagram illustrating the relationship between potential energy curves and eigenquantum defect functions and the procedure by which the eigenquantum defect functions may be determined from potential energy curves. The internuclear distance dependence of the eigenquantum defects governs the shape of the potential energy curves; if the quantum defect is independent of internuclear distance, the potential curve will be parallel to that of the free ion core. If the quantum defect depends substantially on internuclear distance, the potential energy curve will be somewhat distorted.

3.3 Open Ionization Channels: Autoionization and Photoionization

Quantum defect theory is useful not only in describing bound states, but also in describing continuum processes. In quantum defect theory, the presence of a continuum implies the existence of an "open channel". When a channel is open, the motion of the system along at least one coordinate is unbounded while it occupies that channel. The process of autoionization, for example, involves vibronic coupling between an otherwise bound Rydberg state and a lower ionization continuum [11-13]; the Rydberg electron takes up some of the vibrational and/or rotational energy of the ion core and is spontaneously ejected. Photoionization and associative ionization are other examples of processes that involve open ionization channels.
At least conceptually, the theory needs little modification in order to handle open ionization channels; quantum defect theory “naturally” handles bound and unbound radial motion. The main difference lies in the boundary conditions. Unlike the case when all channels are closed and all eigenstates are strictly bound, the wavefunction does not vanish at infinite electron-ion separation. Instead, the wavefunction conforms to what is known as the “outgoing wave” boundary condition [2, 4]. This means that, at infinite electron-ion separation, the wavefunction must be a particular linear combination of Coulomb scattering waves, whose relatives amplitudes are determined by the scattering matrix S. This is discussed extensively in References [2], [4], and [14-17]. The end result, upon imposition of these boundary conditions, is again a homogeneous system of equations:

\[
\left[ \mathbf{K} + \mathbf{T}^{(\rho)} \right] \mathbf{B}^\rho = 0
\]  

(3.20)

in which

\[
T_{ij}^{(\rho)} = \begin{cases} 
(\tan \pi \nu_i) \cdot \delta_{ij} & (\text{closed channels}) \\
(-\tan \pi \tau_{\rho}) \cdot \delta_{ij} & (\text{open channels}) 
\end{cases}
\]

(3.21)

Here, the $\tau_{\rho}$ are called “eigenphases”, and govern the electron radial phase shifts above the ionization threshold in much the same way that the eigenquantum defects $\mu_a$ govern the phase shifts below the ionization threshold. The system (3.20) is solved by finding the roots of the determinant of the coefficient matrix,

\[
\det \left[ \mathbf{K} + \mathbf{T}^{(\rho)} \right] = 0.
\]

(3.22)

Above the ionization threshold, there is of course an eigenstate at every energy, and at any given energy there are as many solutions to (3.20) (and thus as many eigenphases $\tau_{\rho}$) as there are open channels.
The differential oscillator strength, which is proportional to the absorption cross section, into any given open channel is then calculated according to [2, 4, 14-17]

\[
\frac{df}{dE} = 2\omega \left| \sum_{\rho} e^{i\pi\tau_{\rho}} V_{\rho} \sum_{j,j'} B_{j,j'}^{(\rho)} \{ v'_j, f \} \sum U_{j,\alpha}(R) d_{\alpha}(R) v'' \right|^2
\]

(3.23)

and the coefficients \( V_{j,\rho} \) are calculated using the relationships

\[
\sum_j K_j B_j^{(\rho)} \sin \pi\tau_{\rho} + B_j^{(\rho)} \cos \pi\tau_{\rho} = V_{j,\rho},
\]

(3.24)

\[
\forall i \in \{ P \}: \sum_j K_j B_j^{(\rho)} - B_j^{(\rho)} \tan \pi\tau_{\rho} = 0,
\]

(3.25)

and

\[
V^T V = 1.
\]

(3.26)

Here, \( d_{\alpha}(R) \) represent the (internuclear distance-dependent) dipole transition amplitudes between the initial state and each eigenchannel. In CaF, for example, this might be the transition amplitude between the D \( ^3\Sigma^+ \) state and a Rydberg state in the 0.55 \( ^3\Sigma^+ \) Rydberg series.

### 3.4 Open Dissociation Channels: Photodissociation and Dissociative Recombination

Although quantum defect theory was primarily devised to account for the structure of bound Rydberg states and their interactions with the ionization continuum, it is possible to modify the theory to account for the effects of unimolecular dissociation as well. A perturbative approach has been developed by Giusti [18], Giusti-Suzor and Jungen [19], and Raoult [20]. The utility of this approach is that it expresses the interactions
between the Rydberg series and the valence states that dissociate them in terms of the same electrostatic coupling matrix elements that give rise to the avoided crossings between the diabatic Rydberg and valence potential energy curves. The molecular Hamiltonian is divided into three terms:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} + \hat{H}^{(2)}$$  \hspace{1cm} (3.27)

$\hat{H}^{(0)}$ denotes the usual zero-order Hamiltonian $\hat{H}_{\text{Coulomb}} + \hat{H}_{\text{Core}}$, $\hat{H}^{(1)}$ denotes the part of $\hat{H}^{(0)}$ which gives rise to the interactions between Rydberg states, and $\hat{H}^{(2)}$ denotes the part of $\hat{H}^{(0)}$ that gives rise to interactions between the Rydberg and valence states. Accordingly, the reaction matrix $\mathbf{K}$ is divided into two portions; $K^{(1)}$ describes all interactions among Rydberg states, and $K^{(2)}$ describes the Rydberg-valence interactions. The channel functions, which are normally written as

$$\psi_i = f_i(v_i)|i\rangle \delta_j - \sum_j g_j(v_j)K_{ji}|j\rangle,$$  \hspace{1cm} (3.28)

are instead written as

$$\Psi = \sum_j |j\rangle \sum_i [f_i(v_i)C_{ij} - g_jS_{ij}B_i]$$  \hspace{1cm} (3.29)

for convenience. The quantities $C_{ij}$ and $S_{ij}$, in analogy to the long-range reaction matrix elements $K_{ij}$, are given as

$$S_{\lambda N^+,\nu N^+,\nu'} = \sum_\lambda \langle N^+ | \Lambda \rangle \left[ \int \chi^{(\nu)}_{\nu'}(R) \sum_\alpha \langle \ell | \alpha \rangle \sin \mu_{\alpha}(R) \langle \alpha | \ell' \rangle \chi^{(\nu')}_{\nu'}(R) dR \right] \langle \Lambda | N^+ \rangle$$  \hspace{1cm} (3.30)

and

$$C_{\lambda N^+,\nu N^+,\nu'} = \sum_\lambda \langle N^+ | \Lambda \rangle \left[ \int \chi^{(\nu)}_{\nu'}(R) \sum_\alpha \langle \ell | \alpha \rangle \cos \mu_{\alpha}(R) \langle \alpha | \ell' \rangle \chi^{(\nu')}_{\nu'}(R) dR \right] \langle \Lambda | N^+ \rangle.$$  \hspace{1cm} (3.31)

Note that the matrices $\mathbf{S}$, $\mathbf{C}$, and $\mathbf{K}$ are related through
\[ K = S(C^{-1}). \] (3.32)

In the perturbative treatment of molecular dissociation, the set of channels \( i \) is augmented to include the dissociation continua \( d \) as separate channels; i.e. \( i, j \in \{ v^+, d \} \). Neglecting molecular rotation, the part of the reaction matrix due to Rydberg-Rydberg interactions, \( K^{(1)} \), is given by

\[ K^{(1)}_{v', v}, = \int \chi_{v'}(R) \pi \mu_{\alpha}(R) \chi_{v'}(R) dR, \]

\[ K^{(1)}_{v', d} = K^{(1)}_{d', v} = 0, \] (3.33)

while \( K^{(2)} \), the portion due to Rydberg-valence interactions, is given by

\[ K^{(2)}_{v', d} = -\pi V_d \int \chi_{v'}(R) \chi_d(E, R) dR, \]

\[ K^{(2)}_{v', v} = K^{(2)}_{d', d} = 0. \] (3.34)

Here, \( V_d \) is the n*-descaled electrostatic coupling parameter that governs the strength of the avoided crossings between the Rydberg and valence potential energy curves. The structure of this matrix is shown schematically in Figure 3-3. As equations (3.33) and (3.34) imply, if multiple dissociation continua are present, it is assumed that they do not interact. The channel functions are accordingly generalized to include the possibility of motion along the dissociation coordinate:

\[ \Psi = \sum_j \phi_j \sum_\beta \left[ f_j(\varepsilon_j) C_{j\beta} - g_j(\varepsilon_j) S_{j\beta} \right] A_\beta. \] (3.35)

In Eq.(3.35), the functions \( f \) and \( g \) represent the portion of the channel wavefunction that accounts for motion along the generalized “radial” coordinate. For the ionization channels, this coordinate is \( r \), the electron-ion separation. For the dissociation channels, this coordinate is \( R \), the internuclear distance. Accordingly, the functions \( \phi_j \) represent the portions
of the wavefunction corresponding to all degrees of freedom other than the
generalized radial coordinate. For the ionization channels, this $\phi_i$ includes
the angular wavefunction of the Rydberg electron and the vibrational
wavefunction of the ion core, and for the dissociation channels $\phi_i$ includes
the electronic wavefunction of the entire molecule. The quantities $C_{j\rho}$ and
$S_{j\rho}$ are given by

$$C_{\nu \rho} = \sum_{\nu'} \langle \nu' | \beta \rangle \int \chi_{\nu'}(R) \cos \pi \left[ \mu_{\rho}(R) + \mu_{\beta} \right] \chi_{\nu}(R) dR$$

(3.36)

and

$$C_{d\rho} = \langle d | \beta \rangle \cos \pi \mu_{\beta}.$$  

(3.37)

Imposition of boundary conditions gives rise to the homogeneous set of
equations

$$\sum_{\rho'} \left[ \sin \pi \xi C_{j\rho} + \cos \pi \xi S_{j\rho} \right] A^{(\rho')}_{\beta} = 0,$$

(3.38)

in which $\xi = \nu \rho$ for all closed channels and $\xi = -\tau \rho$ for all open channels. In
matrix form, Eq. (3.38) is written as

$$[\sin \pi \xi C + \cos \pi \xi S] A^{(\rho)}_{\beta} = 0,$$

(3.39)

which may be solved using standard linear algebraic techniques. The partial
Figure 3-3: Schematic diagram illustrating the structure of the reaction matrix $K$ when dissociation channels are included in the treatment.

The differential oscillator strength into channel $i$, \( \frac{df}{dE_i} \), may then be calculated, in analogy to (3.23), according to

\[
\frac{df}{dE_i} = \frac{2}{3} \hbar \left| \sum_{\rho} \langle i | \rho \rangle \exp(i \pi \tau_{\rho}) D_{\rho} \right|^2 , \tag{3.40}
\]

in which

\[
\langle i | \rho \rangle = \sum_{\alpha} \left( \cos \pi \tau_{\rho} C_{i\alpha} + \sin \pi \tau_{\rho} S_{i\alpha} \right) A^{(\rho)}_{\alpha} . \tag{3.41}
\]

The only restriction on the use of this method is that, since it is a perturbative treatment, the Rydberg-valence interactions must not be too strong. This simply means that in order for the treatment to remain valid, the system must conform reasonably well to the diabatic picture. This is
generally the case, for example, in NO and CaF. The treatment cannot be used when the interactions between Rydberg and valence states are strong and the adiabatic picture is more appropriate, as is typically the case in H₂.

Interestingly, this treatment also readily lends itself to the calculation of dissociative recombination cross sections [21-24]. This is because the scattering matrix S is directly related to the reaction matrix K,

\[ S = (1 - iK)^{-1} (1 + iK), \]  

(3.42)

and all dissociative recombination cross sections can be calculated directly from S. The cross-section for recombination from the \( \ell, N^*, v^* \) channel is

\[ \sigma_{d, \ell, N^*, v^*} (\varepsilon) = g \frac{\pi}{\hbar^2} \left| S_{d, \ell, N^*, v^*} (\varepsilon) \right|^2. \]  

(3.43)

Mechanisms for dissociative recombination are shown in Figure 3-4, and the structure of the S matrix is shown schematically in Figure 3-5.

**Figure 3-4**: Schematic diagrams illustrating dissociative recombination mechanisms. In the direct mechanism, the ionization continuum (\( AB^+ + e^- \)) is directly coupled to the dissociation continuum (A+B). In the indirect mechanism, the ionization continuum is indirectly coupled to the dissociation continuum through an intermediate Rydberg states, denoted \( AB^* \).
3.5 Unified Treatment of All Scattering

Phenomena

Although the perturbative treatment outlined in Section 3.6 can only be used in the limit that the Rydberg-valence interactions are weak, Jungen and co-workers [25-28] have devised a method whereby all scattering processes may be treated on equal footing, however strong. This partially alleviates the need for computationally expensive electronic structure calculations. This treatment uses a technique borrowed from R-matrix theory to form a vibrationally complete basis for the treatment of dissociation. As shown in Figure 3-6, the core is now given two boundaries;
one at \( r = r_c \) and another at \( R = R_c \). When the system lies in the region \( r > r_c \), it is ionized; when the system lies in the region \( R > R_c \), it is dissociated.

\[ r (\text{electronic motion}) \]
\[ R_c \]
\[ \text{reaction zone} \]
\[ R_c \] \( \text{R (nuclear motion)} \]

Figure 3-6: Diagram showing reaction zones and coordinates relevant to the simultaneous description of ionization and dissociation. Figure adapted from Figure 2 of Reference [19].

The treatment begins in the eigenchannel picture, in which the channel functions are expressed as

\[
\psi_\alpha = \sum_i \Phi_i(\varepsilon) U_{i,\alpha} \left[ f_i(\varepsilon, r) \cos \pi \mu_x - g_i(\varepsilon, r) \sin \pi \mu_x \right].
\]  

(3.44)

The full molecular wavefunction is expressed as a sum over eigenchannel functions, i.e. \( \Psi = \sum_\alpha A_\alpha \psi_\alpha \), and boundary conditions are imposed.

In this case, the boundary conditions are, for closed channels \( i \in Q \),

\[
\forall i \in Q: \quad \psi_\alpha \bigg|_{r \to \infty} \to 0
\]  

(3.45)
and for open channels \((i \in P)\),

\[
\forall i \in P: \quad \psi_{\alpha} \bigg|_{r \to \infty} \to \sum_{i \in P} T_{i,\alpha} \left[ f_i(\varepsilon, r) \cos \pi \tau_{\alpha} - g_i(\varepsilon, r) \sin \pi \tau_{\alpha} \right] \Phi_i(\omega) \quad (3.46)
\]

for open ionization channels, and

\[
\forall d \in P: \quad \psi_{\alpha} \bigg|_{r \to \infty} \to \sum_{d} T_{d,\alpha} \left[ F_d(E, R) \cos \pi \tau_{\alpha} - G_d(E, R) \sin \pi \tau_{\alpha} \right] \Phi_d(\omega) \quad (3.47)
\]

for the open dissociation channels.

Equations (3.46) and (3.47) show the appropriate forms of the wavefunctions in the asymptotic regions, but as yet the phase shifts \(\pi \tau_{\alpha}\) and coefficients \(T_{i,\alpha}\) appearing in the equations are unknown. While the coefficients and phase shifts appearing in Eq. (3.46) are largely determined by the long-range reaction matrix \(K\) and can be calculated using the formalism presented in Section 3.5, the procedure for determining the dissociation phase shifts is slightly more complicated.

The main problem is that it is not known \textit{a priori} where the valence state causing the dissociation is, nor is it known how to describe the dissociation process at short range. Junge and co-workers address this problem by the following procedure: (i) treat the dissociative valence state as a core-excited Rydberg state, (ii) solve for two sets of wavefunctions at \(R < R_0\), (iii) use the superposition principle to match these to the known forms of the wavefunctions in Eq. (3.47), (iv) solve for phase shifts and calculate spectrum.

Since we are treating the valence state as a member of a core-excited Rydberg series (see Fig. 3-7), there are likewise a set of quantum defect matrix elements describing their structure and interactions with the other Rydberg channels. There are diagonal elements, \(\mu_{\alpha,\alpha}^{(n)}(R)\), which describe
the shape of the potential energy curve of the state, as well as off-diagonal elements \( \mu_{\lambda}^{\lambda}(R) \), which describe the interactions with other channels. These additional quantum defects are treated as adjustable parameters to be determined by comparison between theory and experiment.

**Figure 3-7:** Schematic diagram illustrating how a genuine valence state may be effectively treated as a core-excited Rydberg series.
Once these parameters are assigned values, the next step is impose an artificial boundary at $R < R_0$ and perform two separate quantum defect calculations to find a set of eigenstates for which the logarithmic derivative $s - b(R_0)$ of the vibrational wavefunctions,

$$-b(R_0) = \frac{\chi'(R_0)}{\chi(R_0)}, \quad (3.48)$$

assume two separate constant, known values. This is shown schematically in Figure 3-8. Two sets of wavefunctions with two different values of the logarithmic derivative are needed so that any dissociation phase shift can be achieved by superposition. These two sets are distinguished using an additional index $x$:

$$\psi_{\rho}^{(x)}(R \leq R_0) = \sum f_i(\varepsilon,r)\Phi_i(\omega) - \sum K_{ij}^{(x)}g_j(\varepsilon,r)\Phi_j(\omega) \quad (3.49)$$

A general eigenchannel function, for $R < R_0$, is then written as

$$\Psi_{\beta} = \sum_{\rho,x} C_{\rho}^{\beta(x)} \psi_{\rho}^{(x)}(R \leq R_0). \quad (3.50)$$
Figure 3-8: Schematic diagram illustrating the influence of the value of the logarithmic derivative on the vibrational wavefunction. The logarithmic derivative is essentially a quantity that is used to assure that the short-range and long-range forms of the wavefunction are joined properly (i.e. that the combined nuclear wavefunction is continuous and differentiable at $R = R_0$.)

The two forms of the wavefunction [$R \leq R_0$, Eq. (3.49)] $R \geq R_0$, Eq. (3.47)] must be equal at $R = R_0$. Using Equations (3.48) and (3.47), the logarithmic derivative may be expressed as

$$-b^{(x)} = \frac{F_d'(R_0)\cos \pi \tau_d^{(x)} - G_d'(R_0)\sin \pi \tau_d^{(x)}}{F_d(R_0)\cos \pi \tau_d^{(x)} - G_d(R_0)\sin \pi \tau_d^{(x)}}.$$  

Since the logarithmic derivatives are known, this serves to determine the dissociation phase shifts $\tau_d^{(x)}$. The $R \geq R_0$ form of the wavefunction Eq.(3.49)
is then projected onto the $R \leq R_0$ form of the wavefunction [Eq. (3.47)],

which, after some manipulation, gives the coefficients $T_{d\rho}^{(x)}$,

$$T_{d\rho}^{(x)} = \frac{\sum_{\nu, N^+} Z_d^{(x)} \langle R_0 | \nu^+ \rangle \langle \Lambda | N^+ \rangle}{n_d^* (R_0) \left[ F_d (R_0) \cos \pi \tau_d^{(x)} - G_d (R_0) \sin \pi \tau_d^{(x)} \right]}.$$  \hfill (3.52)

To find the actual phase shifts $\pi \tau_a$ and coefficients, $T_{i, \alpha}$, the two asymptotic forms of the wavefunction,

$$\psi_a |_{R \to \infty} \to \sum_d T_{d, \alpha} \left[ F_d (E, R) \cos \pi \tau_a - G_d (E, R) \sin \pi \tau_a \right] \Phi_d (\omega), \hfill (3.53)$$

and

$$\psi_a |_{r \to \infty} \to \sum_{i, \alpha} T_{i, \alpha} \left[ f_i (\varepsilon, r) \cos \pi \tau_a - g_i (\varepsilon, r) \sin \pi \tau_a \right] \Phi_i (\omega), \hfill (3.54)$$

are equated with a short-range expansion of the wavefunction in terms of eigenchannel functions:

$$\Psi_\beta = \sum_{\rho, \pi} c_\rho^{\beta (x)} \psi_\rho^{(x)} (R \leq R_0). \hfill (3.55)$$

Once values for these parameters have been determined, an effective reaction matrix is calculated according to

$$K_{\beta'} = \sum_{\beta} T_{j, \beta} \tan (\pi \tau_\beta) T^*_{\beta', \beta'}, \hfill (3.56)$$

and partial differential oscillator strengths are calculated according to the procedure outlined in Section 3.7.

An example is shown here for $H_2$ [25], in which the $5p\Sigma$ and $4p\Pi$

Rydberg states are adiabatically predissociated by the lower-lying $3p\Sigma$ and

$2p\Pi$ states, as well as preionized by the $\nu = 0$ and $\nu = 1$ ionization continua

[25]. Partial differential oscillator strengths for dissociation into the two
dissociation channels, as well as oscillator strengths for photoionization, are shown in Figures 3-9 and 3-10.

The two advantages of this formalism are that (i) the treatment is not perturbative, and can be used no matter how strong the Rydberg-valence interactions are, and that (ii) the treatment truly does unify electronic structure by treating all electronic states on equal footing.
Figure 3-9: Partial differential oscillator strengths, into both ionization and dissociation channels, in the vicinity of two nominally bound Rydberg states in H₂. (a) Dissociation of 5pΣ v=4. (b) Dissociation of 4pΠ v=5. Calculations performed using programs written by Christian Jungen. All relevant theory, data, and calculations were originally conceived by Jungen and others and published in References [25] through [27].
3.6 Connection with Effective Hamiltonian Theory

While quantum defect theory is exceedingly useful in describing Rydberg states, and can simultaneously treat interactions between an arbitrarily large number of energy levels, numerous insights can be obtained by establishing a connection between QDT and the common Hamiltonian treatments.
In effective Hamiltonian theory, the observed molecular eigenstates are treated as eigenstates of a simpler Hamiltonian, \( H^{(0)} \), which subsequently experience perturbations by an operator \( H^{(1)} \). The resulting eigenstates are often assigned “parentage” in terms of the eigenstates of \( H^{(0)} \) by determining the eigenstate’s largest fractional character. For small perturbations, this serves to establish the basic identity of an eigenstate and helps to convey some of its properties.

This is often not directly possible in quantum defect theory, since there really is no “basis”. The channel mixing amplitudes \( B_{\ell N} \) or \( A_{\ell\lambda} \), defined in the previous sections, serve this purpose to some extent, and typically indicate the dominant character of the eigenstate when the reaction matrix is diagonal or nearly diagonal in either representation. However, when the reaction matrix is highly off-diagonal, which is frequently the case in molecules such as CaF, assignment of fractional character is not as straightforward.

As Altunata [29] has shown, this problem can be addressed by re-expanding the molecular wavefunctions in terms of a new set of channel functions which behave more like the basis states of an effective Hamiltonian treatment. The new channel functions, which we denote here by \( \overline{\psi}_{\ell N'} \), behave much like the asymptotic channel functions \( \psi_{\ell N'} \) described in Section 3.1, but with a few important differences. The new expansion is written as

\[
\Psi(E) = \sum_{\ell, N'} C_{\ell N'}(E) \overline{\psi}_{\ell N'}(E), \tag{3.57}
\]

and the new channel functions are

\[
\overline{\psi}_{\ell N'} = \left[ f_{\ell}(\nu_{N'}(E)) \cos(\pi \mu_{\ell N'}) - g_{\ell}(\nu_{N'}(E)) \sin(\pi \mu_{\ell N'}) \right] \Phi_{\ell N'}. \tag{3.58}
\]
The new channel mixing amplitudes $C_{\ell N^+}$ are related to the original channel mixing amplitudes $B_{\ell N^+}$ through

$$C_{\ell N^+} = B_{\ell N^+} \sec(\pi \mu_{\ell N^+}),$$  \hspace{1cm} (3.59)

in which $\mu_{\ell N^+}$ is defined through the relationship

$$\tan(\pi \mu_{\ell N^+}) = \frac{\sum_{CN^+,CN^+} B_{CN^+,CN^+} K_{CN^+,CN^+}}{B_{\ell N^+}}.$$  \hspace{1cm} (3.60)

The utility of this new expansion is that each channel function $\psi_{\ell N^+}$ is now expressed as a product of a single phase-shifted radial function and an angular function, in which the phase shift of the radial part is given by $\pi \mu_{\ell N^+}$. The fractional characters of the wavefunctions, expressed in terms of $\ell$ and $N^+$, may now be calculated according to

$$P_\ell = \sum_{N^+} C_{\ell N^+}^2,$$

and

$$P_{N^+} = \sum_\ell C_{\ell N^+}^2.$$  \hspace{1cm} (3.62)

The redefinition of the channel functions and channel mixing amplitudes, according to (3.58) and (3.59) respectively, is necessary because the original set of channel functions are not expressed as a product of a single radial function and a single angular function with the same set of quantum numbers. This means that the $B_{\ell N^+}$ coefficients do not behave quite like the basis set mixing coefficients of a Hamiltonian treatment. This invalidates the use of the $B_{\ell N^+}$ coefficients as indicators of the fractional character of the eigenstates. When expressed in terms of the original
asymptotic channel functions, the projection of the angular part of a given channel function onto the full molecular wavefunction yields

\[
\langle \Phi_{\ell^N}^{(N)} | \Psi(E) \rangle = \sum_{\ell^{N^*}} B_{\ell^{N^*}} \left( f_{\ell} \left( \nu_{N^*} \left( E \right) \right) \delta_{\ell^{N^*}, \ell^{N^*}} - g_{\ell} \left( \nu_{N^*} \left( E \right) \right) K_{\ell^{N^*}, \ell^{N^*}} \right),
\]

(3.63)

or

\[
\langle \Phi_{\ell^N}^{(N)} | \Psi(E) \rangle = B_{\ell^{N^*}} f_{\ell} \left( \nu_{N^*} \left( E \right) \right) - \left( \sum_{\ell^{N^*}} B_{\ell^{N^*}} K_{\ell^{N^*}, \ell^{N^*}} \right) g_{\ell} \left( \nu_{N^*} \left( E \right) \right).
\]

(3.64)

The presence of the sum in equation (3.64) is the source of the problem: the coefficient of the irregular Coulomb function contains contributions from channels other than the channel we intended to project out, and the coefficient \( B_{\ell^{N^*}} \) cannot be factored out of the expression. What we desire instead is an expansion of the wavefunction that behaves more like a hydrogenic electron/ion product basis set of the form

\[
\bar{\psi}_{\ell^{N^*}} = R_{n^l} \left( \nu_{N^*} \left( E \right) \right) \Phi_{\ell^{N^*}}^{(N)},
\]

(3.65)

and which satisfies

\[
\langle \Phi_{\ell^N}^{(N)} | \Psi(E) \rangle = C_{\ell^{N^*}} R_{n^l} \left( \nu_{N^*} \left( E \right) \right),
\]

(3.66)

where \( R_{n^l} \left( \nu_{N^*} \left( E \right) \right) \) is a single phase-shifted radial wavefunction referenced to a single rotational energy level of the free ion core. The expansion of the full molecular wavefunctions in terms of the modified channel functions of Eq. (3.58) achieves precisely this separation. The analogous projection in this case yields

\[
\langle \Phi_{\ell^N}^{(N)} | \Psi(E) \rangle = C_{\ell^{N^*}} \left[ f_{\ell} \left( \nu_{N^*} \left( E \right) \right) \cos \left( \pi \mu_{\ell^{N^*}} \right) - g_{\ell} \left( \nu_{N^*} \left( E \right) \right) \sin \left( \pi \mu_{\ell^{N^*}} \right) \right],
\]

(3.67)

which corresponds exactly to the desired form.

This formalism will be used extensively in Chapter 6 in the discussion of resonance phenomena.
3.7 Quantum Defects

Although in the above discussion we have been using the standard (and most common) \( \mu \) quantum defects, other formulations of quantum defect theory, using different base pairs and phase shifts, exist [3] and are in fact preferable under certain circumstances. This section discusses the advantages and disadvantages of each choice of quantum defect.

3.7.1 \( \mu \) Defects

By far the most common form of quantum defect theory in use is the form described above, which employs \( f \) and \( g \) radial wavefunctions and uses the standard \( \mu \) quantum defects. Its main advantage is that the relationship between the quantum defects and the energy levels is maximally transparent. In the single-channel case, the relationship is given by the Rydberg formula. In the multiple-channel case, they are given by the formula \( \det \left| \mathbf{P}(E) + \mathbf{K} \right| = 0 \). Although, in the multiple channel case, the positions of the energy levels are not given by a simple expression like the Rydberg formula, it is often still possible to use the Rydberg formula as a rough guide. This occurs, for example, near the ionization threshold. When the off-diagonal elements of the long-range reaction matrix are small relative to the difference in the corresponding diagonal elements, the channel couplings become negligible and the energy level positions are mainly governed by the diagonal elements. Under these circumstances the system approximately regains the structural simplicity of the single-channel treatment.
The main disadvantage of this formalism is that the $\mu$ defects can produce unphysical behavior at low $n^*$. In particular, the $\mu$ defect formalism does not respect the rule that $n^*$ must be greater than $\ell$, and therefore the formalism cannot be used at energies where $n^* < \ell_{\text{max}} + 1$ [3, 30-32]. If, for example, the calculation includes couplings between channels with $0 \leq \ell \leq 3$, fictitious electronic states with $\ell \geq n^*$ (i.e. 3f, 2d, etc.) can appear in the energy range below the 4f level. Worse, this effect cannot be remedied simply by ignoring these fictitious energy levels: they not only appear in the spectrum, but they also perturb the energy levels which are actually supposed to be there.

3.7.2 $\eta$ Defects

Another quantum defect formalism, using what are known as the $\eta$ defects, is also in common use and overcomes some of the disadvantages of the $\mu$ defect formalism. In particular, the $\eta$ defect formalism does respect the $n^* > \ell$ rule, and therefore can be used across the entire spectrum of the molecule, all the way down to the ground electronic state. The $\eta$ defects are also (at least for atoms) less strongly energy-dependent, which further facilitates their use at low $n^*$ where the binding energy of the Rydberg electron is quite large and the energy dependence of the quantum defects becomes most apparent.

The $\eta$ defect formalism is discussed in detail by Seaton [3], and has been used in the analysis of $\text{H}_2$ in [30-32]. In this formalism, the regular and irregular Coulomb functions $f$ and $g$ are replaced by an alternate set, usually called $f$ and $h$ (note that the f functions of the $\eta$ defect formalism are
generally not the same functions used in the μ defect formalism). The reaction matrix K of the μ defect formalism is accordingly replaced by an alternate reaction matrix Y, whose matrix elements are defined according to

$$Y_{ij} = A_i^l K_{ij} A_j^l.$$  \hspace{1cm} (3.68)

The functions $A_i$ serve to both eliminate the false electronic states that can arise at low $n^*$ as well as to reduce the energy dependence of the reaction matrix elements. They are defined by

$$A_i = \frac{1}{\nu_i^{2\ell+1}} \frac{\Gamma(v_i + \ell + 1)}{\Gamma(v_i - \ell)}.$$  \hspace{1cm} (3.69)

The $A_i$ are exactly zero when $\ell \geq n^*$, forcing the corresponding matrix element of Y to be zero and eliminating the possibility of an unphysical bound state at such an energy. Typically, and especially for the core-penetrating states of atoms, the μ defects decrease with increasing total energy (i.e. increase with increasing binding energy). The functions $A_i$ partially compensate this behavior; the $A_i$ have unit amplitude at the ionization threshold and approach zero as the total energy decreases (i.e. as the binding energy increases).

The channel functions of the η defect formalism take the form

$$\psi_{\ell v' N^*} = \left[ \sum_{v' N^*} Y_{\ell v' N^*; \ell v'' N''} \Phi_{\ell v'' N''}^{(N)} \right] \chi_{\ell v''}^{N''} \Phi_{\ell v''}^{(N)},$$  \hspace{1cm} (3.70)

where the rovibronic Y matrix is calculated according to

$$Y_{\ell v' N^*; \ell v'' N''} = \sum_{\Lambda} \langle \Lambda | N^* \rangle \langle \Lambda | N'' \rangle \left[ \int \chi_{\ell v''}^{N''} (R) \tan(n^{(N)}(R)) \chi_{\ell v''}^{N''} (R) \, dR \right] \langle N'' | \Lambda \rangle.$$  \hspace{1cm} (3.71)
The application of suitable boundary conditions leads, when all channels are closed, to the quantization condition

$$\left[ \frac{\tan \pi \tilde{v}}{A} + Y \right] \tilde{M} = 0 . \quad (3.72)$$

Note that in this formalism, the short range reaction matrix is calculated as

$$Y = \tan \pi \eta . \quad (3.73)$$

The main disadvantage of the $\eta$ defect formalism is that, owing to the presence of the $A$ functions in Eq. (3.69), the relationship between the quantum defects and the energy levels is not as clear as it is in the $\mu$ defect formalism.

The correspondence between Seaton's notation [3] and the notation more commonly used [1] can lead to some confusion, and is most certainly worth mentioning. Seaton's $\mu$ defect formalism uses regular and irregular functions "s" and "c", which are identical to the functions "f" and "g" in common use and which are used here. Likewise, his long-range reaction matrix, written $R$, is identical to the long-range $K$ matrix used here. In matrix form, Seaton's functions are written

$$\psi = s + cR , \quad (3.74)$$

and these functions are identical to our functions

$$\psi = f + gK . \quad (3.75)$$

Seaton's short-range reaction matrix $R$ is likewise identical to our short-range reaction matrix $K$:

$$R = K = \tan \pi \mu . \quad (3.76)$$

In Seaton's $\eta$ defect formalism, Seaton [3] uses "f" and "h" functions:

$$\psi = f + hY , \quad (3.77)$$
which are related to our “f” and “g” functions (or the “s” and “c” functions of Seaton’s \( \mu \) defect formalism) through

\[
s_i = \left( \frac{A_i}{2} \right)^{\frac{3}{2}} f_i \tag{3.78}
\]

and

\[
c_i = \left( \frac{1}{2A_i} \right)^{\frac{3}{2}} h_i \tag{3.79}
\]

The relationship between our long-range matrix \( K \), the \( R \) matrix of Seaton’s \( \mu \) defect formalism, and the \( Y \) matrix of Seaton’s \( \eta \) defect formalism is

\[
Y_\eta = A_j^{\frac{1}{2}} R_j A_j^{\frac{1}{2}} = A_j^{\frac{1}{2}} K_j A_j^{\frac{1}{2}}, \tag{3.80}
\]

where the functions \( A_i \) are all defined according to Eq. xx.

### 3.7.3 \( \bar{\mu} \) and \( \bar{\eta} \) Defects

A potential difficulty in the use of either the \( \mu \) defect formalism of Section 3.7.1 and the \( \eta \) defect formalism discussed in 3.7.2 is that the frame transformation expression

\[
K_{\nu'N'\nu N} = \sum_{\Lambda} \langle \Lambda | N' \rangle^{(N)} \left[ \int \chi_{\nu'}^{N'}(R) \tan \mu_{i\nu'}^{(\Lambda)}(R) \chi_{\nu}^{N'}(R) dR \right] \langle N' | \Lambda \rangle^{(N)} \tag{3.81}
\]

is singular at the point \( \mu = \frac{1}{2} \) [32]. This is of particular concern when the quantum defects are allowed to vary with internuclear distance \( R \) or the binding energy \( \varepsilon \). This difficulty can be removed using the \( \bar{\mu} \) (or \( \bar{\eta} \)) defects, which is discussed in [32]. Using the \( \bar{\mu} \) (or \( \bar{\eta} \)) formalism, an intermediate matrix \( M \) (or \( N \)) is calculated instead according to

\[
M_{\nu'N'\nu N} = \sum_{\Lambda} \langle \Lambda | N' \rangle^{(N)} \left[ \int \chi_{\nu'}^{N'}(R) \bar{\mu}_{i\nu'}^{(\Lambda)}(R) \chi_{\nu}^{N'}(R) dR \right] \langle N' | \Lambda \rangle^{(N)} \tag{3.82}
\]
or

\[ N^{1')(N') = \sum_{\lambda} \langle \lambda | N' \rangle^{(N')} \left[ \int \chi^{N'}_{\nu}(R) \bar{\eta}_{\nu}(R) \chi^{N'}_{\nu'}(R) dR \right] \langle N' | \lambda \rangle^{(N')}. \]  

(3.83)

The final long-range reaction matrices are then calculated according to

\[ K = U \tan \left( \pi U'MU \right) U' \]  

(3.84)

or

\[ Y = U \tan \left( \pi U'NU \right) U', \]  

(3.85)

where U is the matrix which diagonalizes M (or N).

Although the relationships between the \( \bar{\mu} \) (or \( \bar{\eta} \)) and the \( \mu \) (or \( \eta \)) matrices involve several matrix transformations, the eigenquantum defects may be calculated by direct diagonalization of the \( \bar{\mu} \) and \( \bar{\eta} \) matrices themselves:

\[ U^T \mu^{(A)} U = \mu^{(A)}. \]  

(3.86)
3.8 Bibliography


[21] B. Vâlcu, I. F. Schneider, M. Raoult, C. Strömholm, M. Larsson, and


(2000)


Chapter 4

Spectra and Assignment Techniques

4.1 Experimental Apparatus and Techniques

The CaF experimental data described in this thesis were extracted from double-resonance spectra recorded at MIT using the apparatus described in detail by Clevenger [1] and Gittins [2]. Photographs of the apparatus are shown in Figures 4-1 through 4-3. The apparatus consists of a laser ablation/molecular beam source, which is coupled to a time-of-flight mass spectrometer. The molecular beam source and TOF mass spectrometer are housed in separate chambers (termed “source” and “detection” chambers), which are separated by a manually-operated inline gate valve (see detail in Figure 4-4). Although this apparatus was used almost exclusively to record spectra of CaF, it can be easily modified to record spectra of (i) any molecule which exists as a permanent gas, (ii) any molecule which can be prepared as a dilute mixture in an inert gas, (iii) any molecule which can be prepared in situ by UV photolysis, or (iii) any of a large number of metal-containing molecules which can be prepared by photoablation of a metal target rod.
Figure 4-1: Vacuum apparatus used to record double resonance spectra. “a”: source chamber. “b”: Detection chamber. “c”: Pulsed valve driver and vacuum gauge equipment. “d”: Time of flight mass spectrometer. “e”: Molecular beam axis.


In these experiments, a molecular beam of calcium monofluoride is produced in the source chamber by direct reaction of calcium plasma with fluoroform. A 350 µs pulse of 5% fluoroform (CHF$_3$) in helium, formed by a pulsed nozzle (General Valve Series 9, 0.5 mm orifice, 40 psi stagnation pressure, 20 Hz duty cycle), is synchronized with the pulsed production of a calcium plasma, formed by laser ablation of a 0.245” diameter calcium rod by the third harmonic of a pulsed nanosecond Nd:YAG laser. The duration of the fluoroform pulse and the energy of the ablation laser are both adjusted to optimize the production of CaF and to reduce the amount of unreacted calcium. CaF$^+$ ($m/z=59$) is the dominant ion observed, and Ca$^+$ ($m/z=40$) is often observed as well, depending on the laser power used in
Figure 4-4: Schematic drawing showing CaF production, excitation, and detection. (a) Pulsed valve. (b) Calcium rod. (c) Conical skimmers. (d) Ion steering optics. (e) Microchannel plate detector.

the experiments. When the apparatus is operating correctly, and the detector plates are clean and the lasers are well-aligned to the excitation/ionization region, no other ions with greater than a few percent of the intensity of Ca$^+$ are observed.

The molecular beam is collimated by a 0.5 mm conical skimmer placed between the source and detection chambers, and again by a 3.0 mm skimmer prior to entering the excitation region of the detection chamber. Rydberg states are populated and ionized in the detection chamber by two co-linear laser beams that intersect the molecular beam at a 90° angle. The CaF$^+$ ions that result are accelerated down the 75 cm flight tube of the mass spectrometer by a 250 V electric field pulse that arrives 200 ns after the laser excitation pulse. Ions are detected by two microchannel plates (Burle
Electrooptics, 10 µm channel diameter, 12 µm channel spacing) arranged in a chevron configuration. The ion signals are amplified by a low-noise voltage amplifier (FemtoAmp, 30 dB gain, 30 MHz low-pass filter) and averaged over 40 shots by a LeCroy 1 GHz digital oscilloscope. The ion extraction assembly is contained within a Ni-plated shroud to isolate the excitation region from stray electric fields.

4.1.1 Double-Resonance Spectra: Multiphoton Ionization Experiments

Rydberg states in the energy range \( n^* = 5, \nu = 0 \) (total energy approximately 42,500 cm\(^{-1}\)) to \( n^* = 15, \nu = 0 \) (total energy approximately 46,900 cm\(^{-1}\)) lie below the CaF ionization threshold, and must be probed using multiphoton ionization techniques [see Fig. 4-5(a)]. This was typically accomplished using appropriate rovibrational levels of the \( D^2\Sigma^+ \) state as intermediates. The experiments are conducted as above, but typically a very large laser pulse energy must be employed as these Rydberg states are strongly predissociated. The two laser pulses are also partially overlapped in time to maximize the photoionization signal. The wavelength of the fundamental output of the pump and probe dye lasers lies in the deep red portion of the spectrum (600-700 nm) and thus the lasers must be calibrated by simultaneous acquisition of high-temperature absorption spectra of molecular iodine.
Figure 4-5: Energy level diagrams illustrating two main detection methods. (a) Detection by multiphoton ionization. (b) Detection by spontaneous (and perhaps “forced”) autoionization.

4.1.2 Double-Resonance Spectra: Detection by Autoionization

CaF Rydberg states lying above the \( v = 0 \) ionization potential (total energy \( >46,998 \text{ cm}^{-1} \)) are also accessed by two-step excitation through either the \( D^2\Sigma^+ \) or \( F^2\Sigma^+ \) intermediate states [see Fig. 4-5(b)], with the apparatus configured exactly as above, but spectra in this energy range are typically recorded with the probe laser operating at a much lower output power. Above the ionization threshold, all Rydberg states autoionize (i.e. ionize spontaneously without absorption of a second photon), and spectra of excellent quality can be acquired using less than \( \sim 200 \text{ \mu J/pulse} \).

In those spectra for which the \( F^2\Sigma^+ \) state was used in the initial excitation step, a hydrogen Raman shifter was used to generate near-infrared
light for the probe step, since the \( F^{1/2} \Sigma^+ \) state lies only \( \sim 11,000 \text{ cm}^{-1} \) below the ionization threshold. The Raman shifter, when employed, was used in conjunction with a dye laser operating in the deep red (650-700 nm) at full output power (typically greater than 40 mJ). This produces reasonable output power upon Raman shifting: at least 1 mJ in the first Stokes output, and slightly less than 1 mJ in the second Stokes and first anti-Stokes outputs. The second anti-Stokes output was often observed, as was the third harmonic (see Fig. 4-6).

Some autoionization-detected spectra of nonpenetrating Rydberg states are shown in Figure 4-7.

Figure 4-6: Output of Raman shifter, showing the input beam (red), first anti-Stokes output (green) and second anti-Stokes output (blue).
4.1.3 Double-Resonance Spectra: Strategies for Targeting a Class of Rydberg States

The intermediate state used in a particular experiment can have a very dramatic effect on the relative intensities of the various Rydberg series observed in the spectrum. Typically, the A\textsuperscript{2}Π, B\textsuperscript{2}Σ\textsuperscript{+}, and D\textsuperscript{2}Σ\textsuperscript{+} states, all of which have significant s, p, or d character and all of which are of normal polarization [3] and provide very good access to core-penetrating states [2, 4]. The C\textsuperscript{2}Π and F\textsuperscript{'}\textsuperscript{2}Σ\textsuperscript{+} states, on the other hand, have significant d character and are both “reverse-polarized” [2, 4-5]. As a result, the strongest transitions observed in spectra recorded from these two intermediate states terminate on f Rydberg states [2, 4-5]. In spectra recorded from the F\textsuperscript{'} state, g states also appear with reasonable intensities, presumably because (i) the large CaF\textsuperscript{+} core dipole moment produces significant f-g mixing, combined with the fact that (ii) all states with significant f character are easily observed from this intermediate state.

States with high \( \Lambda \) are normally not observed at low \( n^\ast \) \( (n^\ast < 10) \), since for the core-penetrating states \( \ell \)-uncoupling is still rather weak in this range, and only \( \Sigma \) or \( \Pi \) intermediate states are typically used in the experiments. Indeed, the only state with \( \Lambda > 1 \) observed below the ionization threshold is the 9.14 \( \Delta \) state. Above \( n^\ast \approx 10 \), however, \( \ell \)-uncoupling becomes strong enough that core-penetrating \( ^2\Delta \) states can be easily observed. States of \( \Phi \) and even \( \Gamma \) symmetry with \( \ell \geq 3 \) are also commonly observed above the ionization threshold.
Figure 4-7: Typical double resonance spectra, recorded from the F' $^2\Sigma^+$ intermediate state. The strong transitions appearing in this set of spectra terminate on nf Rydberg states. Note the similarity of the spectrum from one $n^*$ to the next.

4.2 Assignment Techniques

Before any spectroscopic data can be analyzed, the transitions appearing in the spectrum must be rigorously assigned. This is best accomplished using rigorous selection rules and information from the spectrum alone, since predictions based on specific models (which can sometimes be overly flexible) can lead to misidentification of transitions, and ultimately, inaccurate conclusions.

Generally, core-penetrating states are quite straightforward to assign, since they usually appear in the spectrum as well-separated electronic states with fairly regular rotational structure [6-7]. Nonpenetrating states, on the other hand, tend to be more difficult in this regard because strong $\ell$-uncoupling causes the core-nonpenetrating states to evolve rapidly from Hund’s case (b) to Hund’s case (d) coupling with increasing rotational excitation [6-9]. This results in unusual and abrupt changes in the rotational energy level patterns, which makes the identification of rotational
branches difficult. Sequential transitions in rotational branches are often
difficult to recognize, and the pattern of intensities can change quite rapidly.

To address these difficulties, a suite of assignment techniques has been
developed, which enables most nonpenetrating states to be assigned with
minimal ambiguity. These techniques, and the ambiguities inherent to their
use, are described here. Most have been discussed previously in [10], and
some in [5].

4.2.1 Core-penetrating states

Because the core-penetrating states conform to Hund’s case (b)
coupling and the valence intermediate states from which the Rydberg states
are excited are described conform to either case (a) or case (b) coupling, the
core-penetrating states appear in double-resonance spectra in rotational
patterns that are relatively simple. The spectra may thus be assigned using
the traditional method of lower-state rotational combination differences.
The ability to assign core-penetrating states in double-resonance spectra by
lower-state rotational combination differences is facilitated by the fact that
Rydberg states are always excited from a rotational level of the intermediate
valence state whose total angular momentum \([J\) in case (a) or \(N\) in case (b)]
and parity [usually indicated as \(\pm\) or \(p = 0,1\)] are known. The rigorous
assignment of core-penetrating Rydberg states is frustrated only when
multiple rotational transitions to a common upper state are unobservable
because of systematic intensity effects. This sometimes occurs when two
adjacent core-penetrating states interact via \(\ell\)-uncoupling, which can lead to
interference effects such as the disappearance of an entire P or R branch.
All of the $^2\Sigma^+$ intermediate states, as well as most members of the six core-penetrating Rydberg series, are well-described by the Hund’s case (b) basis $|n\ell\lambda NSJ\rangle$. The rigorous case (b)—case(b) optical selection rules are

$$\Delta J = 0, \pm 1$$
$$\Delta \Lambda = 0, \pm 1,$$
$$\pm \leftrightarrow \mp$$

and, especially at moderate-to-high $J$, there is a strong propensity rule:

$$\Delta N = 0, \pm 1.$$  \hspace{1cm} (4.2)

A schematic energy level diagram with allowed $^2\Sigma^+ \leftarrow ^2\Sigma^+$ and $^2\Pi \leftarrow ^2\Sigma^+$ transitions is shown in Fig. 4-8. Because $N$, rather than $J$, becomes the pattern-forming quantum number at moderate rotational excitation, transitions are usually designated by $^{\Delta N} \Delta J$ (read “$\Delta N$-form $\Delta J$”; e.g. “P-form Q”).

Spin structure is almost never observed. The spin splittings of Rydberg states of CaF are almost always unresolvable, the only exceptions being the lowest few rotational levels of $^2\Pi$ states with $n^* < 6$. The spin structure of the intermediate states is likewise usually unresolvable, and the only spin effects to be seen are spin-orbit splittings between components of the upper state in $^2\Pi \leftarrow X^2\Sigma^+$ transitions. The small spin-rotation splittings in the $^2\Sigma^+ \leftarrow X^2\Sigma^+$ transitions are completely unresolvable up to $N' \approx 15$. 

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Figure 4-8: Allowed transitions from a $^2\Sigma^+$ intermediate state to $^2\Sigma^+$ and $^2\Pi$ Rydberg states. Transitions which are overlapped in the spectrum, due to unresolved spin structure, are shown overlapped in this diagram. This figure was previously published by the author of this work in reference [10].

Since each rotational level of each core-penetrating state is nominally accessible from at least two rotational levels of any of the intermediate states, rotational assignments of the core-penetrating states can often be made exclusively using lower-state rotational combination differences. Lower-state combination differences are identified by plotting the spectra recorded from each of the rotational levels of the intermediate state against their upper-state “term values”. Term values are calculated as the sum of
the second-photon energy and the total energy of the intermediate rotational level from which they are recorded. These “term value” spectra are then stacked vertically, in order of increasing \( N'' \), and compared against each other to locate lines on separate spectra with identical term values. The observation of two or more lines with the same upper state term value (the same vertical position on the term value stacked plot) suggests the occurrence of transitions from two or more intermediate state rotational levels to a common upper state rotational level. Figure 4-9(a) shows the observed combination differences for a \( ^2\Sigma^+ \leftrightarrow ^2\Sigma^+ \) transition. Rotational levels of \( ^2\Sigma^+ \) and \( ^2\Pi^- \) core-penetrating states are each accessible from two rotational levels of the intermediate \( ^2\Sigma^+ \) states, and rotational levels of \( ^2\Pi^- \) core-penetrating states are nominally accessible from three rotational levels of the intermediate \( ^2\Sigma^+ \) states. However, in our spectra, lower state rotational combination differences are only observed between at most two states on \( N'' \) and \( N''+2 \) spectra, indicating that these states are accessed by O- and Q-, P- and R-, or Q- and S-form transitions. Many of the observed upper states do not exhibit lower-state rotational combination differences. Rotational assignment is more secure for upper states that exhibit lower state rotational combination differences, and these states are usually analyzed first.

After all suspected combination differences have been identified, the spectra are re-plotted against the observed second-photon transition frequency, and stacked vertically in order of increasing \( N'' \) in order to enable organization of the transitions into rotational branches. An example of a \( ^2\Sigma^+ \leftrightarrow ^2\Sigma^+ \) transition is again shown in Figure 4-9(b). The transition frequencies of the members of these rotational branches are each fit to a
polynomial in \( N'' \) to determine \( \Delta N = N'' - N' \) for each branch. The difference \( \Delta N = N'' - N' \) may be derived from the polynomial fit based on the difference in rotational energy between the intermediate state and the core-penetrating states:

\[
\Delta E_{\text{rot}} = v_0 + B' N'(N'+1) - B'' N'' (N''+1).
\]  

(4.3)

The difference in rotational energies is related to the second-photon transition frequency through

\[
\Delta E_{\text{transition}} = \Delta E_{\text{cl}} + \Delta E_{\text{vis}} + \Delta E_{\text{rot}},
\]

(4.4)

where \( \Delta E_{\text{transition}} \) is the second-photon transition frequency. Hence

\[
\Delta E_{\text{transition}} = \Delta E_{\text{rot}} + \text{Const.},
\]

(4.5)

where the constant on the right is independent of \( N \). Using the above equations, combined with the relation \( N' = N'' + \Delta N \),

\[
\Delta E_{\text{transition}} = B'(N'' + \Delta N)(N'' + \Delta N + 1) - B'' N'' (N''+1).
\]

(4.6)

Expanding (7),

\[
\Delta E_{\text{transition}} = N'' (B' - B'') + N'' (B' (2\Delta N + 1) - B'') + B' (\Delta N)^2 + \Delta N).
\]

(4.7)

Since \( N'' \) is known \textit{a priori} from the first step of the double-resonance excitation, and \( B'' \) is known for each intermediate state from previous rotational analyses, the linear term of Eqn. (4.7) yields the difference in rotational quantum number \( \Delta N = N' - N'' \) and the quadratic term yields the effective rotational constant, \( B' \), of the upper state.
Figure 4-9: Portions of spectrum showing (a) location of combination differences and (b) arrangement of transitions into P and R branches, for a $^2\Sigma^+ \leftrightarrow ^2\Sigma^+$ transition. This figure has been previously published by the author of this work in reference [10].

The rotationless upper state quantum defects, $\delta$, are then calculated by inverting the Rydberg formula, using the known vibrational levels of the ion core to establish membership in a core-penetrating series as well as the vibrational quantum number of the Rydberg state in question. The calculated values of $\Delta N$ (and to a lesser extent, $B'$) and comparisons of the calculated rotationless quantum defects with the known quantum defects of the core-penetrating states allow many of the branches that are linked by lower-state rotational combination differences to be conclusively assigned as P- and R-form branches.
The negative Kronig symmetry components of \( ^2\Pi \) and \(^2\Delta \) core-penetrating Rydberg states are assigned by a slightly different strategy. The fact that O-, Q-, and S-form branches are never observed to be linked to the assigned P- and R-form branches through lower-state combination differences, even at low \( n^* \), reveals the presence of interactions which lift the degeneracy of the nominally near-degenerate positive and negative Kronig symmetry components. Sequences of strong, broad lines are often observed in the vicinity of the \(^2\Pi \) and \(^2\Delta \) Rydberg states, and by fitting the observed transition frequencies to the polynomial in Eq. (4.7), it is concluded that these are Q-form branches. Extrapolation of the upper state term values to \( N = 0 \) further indicates that these branches terminate on the negative Kronig symmetry components of the 0.36 \(^2\Pi \) and 0.14 \(^2\Delta \) states. However, no O- or S-form branches terminating on the negative Kronig symmetry components of the 0.36 \(^2\Pi \) or 0.14 \(^2\Delta \) states have ever been observed, due to the weakness of \( \Delta N = 2 \) case (b)—case(b) transitions. While it is thus not possible to rigorously assign the negative Kronig symmetry components of the 0.36 \(^2\Pi \) or 0.14 \(^2\Delta \) states through lower-state rotational combination differences, the assignments are quite secure, as no other rotational branches are expected to be systematically present outside of the near-integer-\( n^* \) region.

Assignments of 0.98 \(^2\Pi \) Rydberg states are invariably frustrated by congestion and spectral overlap due to transitions terminating on core-nonpenetrating states. The 0.98 \(^2\Pi \) Rydberg states are best assigned after definitive assignments of the nonpenetrating Rydberg states are made.
4.2.2 Core-nonpenetrating states

Due to strong $\ell$-uncoupling interactions, the core-nonpenetrating states of CaF evolve rapidly from Hund’s case (b) coupling to Hund’s case (d) coupling, and at even moderate $N$ ($\approx 8$), the core-nonpenetrating states are better-described by the Hund’s case (d) basis, \( |\ell N^+ N \ell_R \rangle \). Core-nonpenetrating states are labeled by $n\ell(\ell_R)^\pm$ (e.g. 17f(-3)$^+$), where $\pm$ refers to the $\sigma_c$ reflection symmetry (Kronig symmetry) of the state, and $\ell_R = N - N^+$. The unique assignment of nonpenetrating Rydberg states involves at the very least the determination of (i) the total angular momentum $N$, (ii) the orbital angular momentum $\ell$, and (iii) one of the remaining three quantum numbers: the projection of $\ell$ along the internuclear axis, $\lambda$, the projection of $\ell$ along the axis of rotation, $\ell_R$, or the total angular momentum of the free ion core, $N^+$.

The case (d)—case (b) selection rules depend to some extent on the mechanism by which the core-nonpenetrating states are accessed from the intermediate state. One mechanism by which nonpenetrating states are observed is \( \text{via} \) on the partial-$\ell$ composition of the intermediate state. If, for example, the intermediate state has significant $\ell = 2$ character, it is possible to observe strong transitions to nf Rydberg states. In this case, the case (d)—case (b) selection rules are

\[
\Delta N = 0, \pm 1
\]

\[
N^+ = |N'' - \ell''| \ldots (N'' + \ell'')
\]

(9)
Here, $\ell''$ represents the orbital angular momentum component of the $\ell$-mixed intermediate state that provides intensity for the transition into the nonpenetrating state, and “±” is the overall parity of the molecular wavefunction, which in case (d) is $(-1)^{N^+ + \ell}$. Core-nonpenetrating states may also be excited due to intensity borrowing from nearby core-penetrating states. In this case, the selection rules are relaxed to

$$\Delta N = 0, \pm 1$$

$$\pm \leftrightarrow \mp .$$

All $N^*$ rotational states with $|\ell'\ell| = N - N^* \leq \ell$ are accessible in this case, provided that the $\Delta N = 0$ core-penetrating-core-nonpenetrating interactions are strong enough to transfer significant intensity into the core-nonpenetrating state.

A schematic energy level diagram, showing transitions between the intermediate state and the nonpenetrating states, is shown in Fig. 4-10. Due to the selection rules on total parity outlined above, only odd (even) rotational levels of even-$\ell$ (odd-$\ell$) states are accessible from odd (even) $N$ levels of a given intermediate state. For example, the $N^* = 3$ level of a g state is inaccessible from the $N = 3$ level of the $D^2\Sigma^-$ state. Because of this parity restriction, many rotational levels of a core-nonpenetrating state are accessible from only one rotational level of the intermediate state, and not all core-penetrating rotational levels can be rigorously assigned through lower-state rotational combination differences.
Figure 4-10. Schematic diagram showing possible transitions from a single rovibrational level of a $^2\Sigma^+$ intermediate state to all possible nonpenetrating Rydberg states. Transitions terminating on states with the same $N^+$ appear narrowly-split in the spectrum. This figure has been previously published by the author of this work in reference [10].
Attempts were made to determine the changes in pattern forming quantum number, $\Delta Q = N^+ - N^-$, from fits of the second-photon transition frequencies, as was done for the core-penetrating states. Substituting $\Delta Q = N^+ - N^-$ for $\Delta N = N' - N''$, one may derive an expression similar to Eqn. (4.7):

$$\Delta E_{\text{Rydberg-}D'\Sigma^+} = N''(B'' - B') + N'(2\Delta Q + 1) - B'' + B'(\Delta Q)^2 + \Delta Q). \quad (4.8)$$

However, for many of the branches, the calculated value of $\Delta Q$ turns out to be approximately half-integral. The reason for non-integer values of $\Delta Q$ is that $\ell$-uncoupling is incomplete at low rotation. The effect of incomplete $\ell$-uncoupling on the value of $\Delta Q$ obtained from a polynomial fit to Eq. (4.8) can be demonstrated using an effective Hamiltonian. The effective Hamiltonian is expressed in a case (b) basis, and is divided into diagonal and off-diagonal terms:

$$H = H^{(0)} + H^{(1)} \quad (4.9)$$

where

$$H^{(0)} = H_{el} + H^{(0)}_{rot} \quad (4.10)$$

and

$$H^{(1)} = H^{(1)}_{rot} = -B(N^+ \ell^- + N^- \ell^+). \quad (4.11)$$

Here, $H_{el}$ is the electronic Hamiltonian, and consists of the Coulomb Hamiltonian and long-range electric dipole and quadrupole interaction terms.

Its matrix elements are

$$\langle n\ell N \lambda | H_{el} | n\ell N \lambda \rangle = \left( E_{\text{ion}} - \frac{\mathcal{R}}{n^2} \right) + \frac{2Z^2}{n^3} \left( \mu^2 - Q \right) \left( \ell (\ell + 1) - 3 \lambda^2 \right) \frac{2 \ell + 1}{(2 \ell + 3)(2 \ell + 1)(2 \ell - 1) \ell (\ell + 1)}. \quad (4.12)$$
$H_{\text{rot}}^{(0)}$ is the diagonal portion of the case (b) rotational Hamiltonian, which has matrix elements

$$\langle n\ell\lambda N | H_{\text{rot}} | n\ell\lambda N \rangle = B \left( N(N+1) + \ell(\ell+1) - \Lambda^2 \right).$$  \hspace{1cm} (4.13)

$H_{\text{rot}}^{(1)}$ is the off-diagonal portion of the rotational Hamiltonian; i.e. the $\ell$-uncoupling operator:

$$H_{\text{rot}}^{(1)} = -B \left( N^+ \ell^- + N^- \ell^+ \right).$$  \hspace{1cm} (4.14)

The eigenvalues of this Hamiltonian can be converted to transition frequencies by subtracting the term value of the rotational level of the intermediate state from which each nonpenetrating state is accessible, and the calculated transition frequencies can be fit to Eqn. (4.8). Plots of the calculated transition frequencies vs. $N''$ are shown in Figs. 4-11 and 4-12.
Figure 4-11: Calculated transition frequencies of transitions terminating on \( n_f \) nonpenetrating states. Branches are labeled using the case (d) quantum numbers \( \ell (\ell_n)^\pm \). This figure has been previously published by the author of this work in reference [10].
Figure 4-12: Calculated transition frequencies of transitions terminating on \( ng \) nonpenetrating states. Branches are labeled using the case (d) quantum numbers \( \ell (\ell_n)^z \). This figure has been previously published by the author of this work in reference [10].
As can be seen in Figs. 4-11 and 4-12, $\ell$-uncoupling alters the calculated $\Delta Q$ values significantly and non-systematically from their actual values, even for calculated data in which the interaction between core-penetrating and core-nonpenetrating states is not accounted for. However, what is apparent from the figures is a clustering of branches in groups of three according to a common value of $N^+ - N^-$. This clustering of branches reflects the fact that $N^+$ is the rotational pattern-forming quantum number in case (d). In Fig. 4-11, the three groups of branches terminating on $nf$ states have $N^+ - N^- = 0, \pm 2$, and in Fig. 4-12 the four groups of branches terminating on $g$ states have $N^+ - N^- = \pm 1, \pm 3$. Superimposing the 17f and 17g transition frequencies (see Figs. 4-13), it is seen that the transitions into the f and g states form a staggered pattern, reflecting the parity selection rules outlined above. The staggered pattern of f and g states in Fig. 4-11 is indeed observed in the double-resonance spectrum (see Figs. 4-13), and allows branches terminating on core-nonpenetrating states to be organized into f and g $N^+ - N^-$ clusters. This allows $N^+ - N^-$ and $\ell$ to be assigned almost by inspection. The only quantum number that remains to be assigned is $N$, and it is often the case that one or two of the branches in a given $N^+ - N^-$ cluster can be linked to another branch by lower-state combination differences.
Figure 4-13: Patterns of transition frequencies for transitions terminating on nonpenetrating Rydberg states. (a) $nf$ states. (b) $ng$ states. (c) $nf$ and $ng$ states superimposed, showing staggering of rotational branches. (d) $nf$, $ng$, and $nh$ Rydberg states. Note that on account of parity, the $nf$ and $nh$ branches lie in similar locations.
These assignment techniques work so well, in fact, that it has been possible to assign whole $f$ and $g$ complexes, and even exceedingly weak transitions to $h$ states. Some examples are shown in Figures 4-14 through 4-16.

Perturbations between core-penetrating and core-nonpenetrating states can also be useful in establishing the identity of nonpenetrating states, especially when the nonpenetrating states appear in fragmentary patterns. Since all operators appearing in the molecular Hamiltonian conserve $N$ (except for the spin-orbit operator, which has a negligible effect on the energy levels in the spectra described here), any state that is perturbed (even slightly) by a core-penetrating state of known $N$ may be assigned a unique of $N$. Since both $N^+ - N^-$ and $\ell$ are relatively straightforward to assign, this typically results in a complete assignment.

Occasionally, and usually only for levels with very low $N(< 5)$, it is nearly impossible to assign $N$ without additional information. Polarization-based intensity measurements [11] can be used in these cases to unambiguously assign $N$. 

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Figure 4-14: Examples of observed Rydberg states. (a) 13f Complex, (b) 15f Complex. Connected blue dots indicate calculated energy levels, and connected red dots indicate observed energy levels.
Figure 4-15: Examples of observed Rydberg states. (a) 13g Complex. (b) 15g Complex. Connected blue dots indicate calculated energy levels, and open red circles indicate observed energy levels.
Figure 4-16: Examples of observed Rydberg states. (a) 13h Complex. (b) 15h Complex. Connected blue dots indicate calculated energy levels, and open red circles indicate observed energy levels.
4.3 Bibliography