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2007

Part 2

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Chapter 5

Quantum Defect Theory Fit of CaF Spectrum

The results of a global fit of the electronic spectrum of CaF is presented in this chapter. Using a specially-tailored fit strategy that employs physical intuition along with a combinatorial computational approach, it has been possible to determine all 20 equilibrium quantum defects, all 20 linear derivatives with respect to internuclear distance, 16 of 20 linear derivatives with respect to electronic collision energy, and 35 of the 60 quadratic derivatives. These values provide a firm basis for understanding both the specific origins of the quantum defects of CaF, as well as provide the basis for a general model that embodies all possible energy transfer mechanisms possible in a diatomic molecule.

5.1 Application of QDT to CaF

The quantum defect theory fit is conducted in the asymptotic formulation described in Section 3.1. The input data includes all electronic states of CaF observed to date with $5 \leq n^* \leq 22$ and $0 \leq \ell \leq 3$. Many of these energy levels were also observed or analyzed in previous work [1-5], and those which were not observed in spectra recorded by this author (mainly levels with $n^* < 6$) were taken directly from these sources. These energy levels span approximately 5000 cm$^{-1}$ and include levels with $0 \leq v \leq 5$ and $0 \leq N \leq 14$. Given this range of quantum numbers and the restrictions
\[ N = \ell + N^* \quad \text{and} \quad p = (-1)^{\ell N^*}, \]
each vibrational channel has ten associated rotational channels with (+) Kronig symmetry and six with (-) Kronig symmetry for each \( N \), which gives a total of 60 channels in all for (+) Kronig symmetry and 36 channels for (-) Kronig symmetry. (Note that although all levels are fit simultaneously, regardless of \( N \), the actual energy level calculations during the course of the fitting procedure can be performed separately for each \( N \).)

Because the fit encompasses such a wide range of parameter space, the quantum defects are allowed linear and quadratic dependences on the internuclear distance and binding energy of the Rydberg electron. The quantum defects are thus expanded as

\[
\mu_{\ell\ell'}^{(\lambda)}(R, E) = \mu_{\ell\ell'}^{(\lambda)}(R) \left|_{\varepsilon=0} \right. + \left. \frac{\partial \mu_{\ell\ell'}^{(\lambda)}(R)}{\partial E} \right|_{\varepsilon=0} \cdot E + \left. \frac{\partial^2 \mu_{\ell\ell'}^{(\lambda)}(R)}{\partial E^2} \right|_{\varepsilon=0} \cdot E^2
\]

\[
\approx \mu_{\ell\ell'}^{(\lambda)}\left|_{R=R^*_c} \right. + \left. \frac{\partial \mu_{\ell\ell'}^{(\lambda)}}{\partial R} \right|_{R=R^*_c} (R - R^*_c) + \left. \frac{\partial^2 \mu_{\ell\ell'}^{(\lambda)}}{\partial R^2} \right|_{R=R^*_c} (R - R^*_c)^2
\]

\[
+ \left. \frac{\partial \mu_{\ell\ell'}^{(\lambda)}}{\partial E} \right|_{\varepsilon=0} \cdot E + \left. \frac{\partial^2 \mu_{\ell\ell'}^{(\lambda)}}{\partial E^2} \right|_{\varepsilon=0, R=R^*_c} \cdot E^2
\]

(5.1)

The subscript \( \varepsilon = 0 \) indicates that the energy derivatives are evaluated at zero binding energy; i.e. at the ionization threshold. Since the quantum defects are allowed variation in both \( R \) and \( E \), it is to be expected that some quantum defects may pass through the value \( \mu = \frac{1}{2} \) at some point. The \( \bar{\mu} \) defects have therefore been employed to circumvent this potential difficulty [5-7]. The quantum defects and their derivatives with respect to \( R \) and \( \varepsilon \),
along with the ionization potential and the structural parameters of the ion core (vibrational frequency, rotational constant, etc.) are all taken as adjustable parameters and are allowed to vary at specific points during the fit process.

5.2 Fit Methodology

The fit itself is conducted in the standard linear least-squares formulation, which is described in [8-9]. The fit was performed using quantum defect theory programs written by Christian Jungen, which were personally communicated to the author of this work. In a linear least-squares fit, the observations $y$ are linearly related to the fit parameters $x$ through the relationship

$$\tilde{y} = A \tilde{x} + \tilde{r}. \tag{5.2}$$

Both $x$ and $y$ are column vectors, and in our case each entry represents a fit parameter (quantum defect, quantum defect derivative, or ion core structural parameter) or an observed energy level, respectively. Here, $r$ represents the "residuals"; the difference between the observed and calculated energy levels. The rectangular matrix $A$ is the first derivative of each energy level with respect to each parameter:

$$A_j = \frac{\partial y_i}{\partial x_j}. \tag{5.3}$$

In the least-squares formulation, the parameters are varied so as to minimize the sum of the squares of the residuals $\Phi$. The sum of the squares is calculated is
\[
\Phi = \sum r_i^2 = \sum r_i \cdot r_i = \mathbf{\hat{r}}^\top \mathbf{\hat{r}}.
\]

\[
= (\mathbf{\hat{y}} - \mathbf{A}\mathbf{\hat{x}})^\top (\mathbf{\hat{y}} - \mathbf{A}\mathbf{\hat{x}}) .
\] 

The minimization of \( \Phi \) is accomplished by differentiating \( \Phi \) with respect to \( \mathbf{x} \) and equating the result with zero:

\[
\frac{\partial \Phi}{\partial \mathbf{x}} = -2\mathbf{A} \mathbf{\hat{y}} + 2\mathbf{A}'\mathbf{A}\mathbf{\hat{x}} \equiv 0.
\]

\[
\Rightarrow \mathbf{A}'\mathbf{\hat{y}} - \mathbf{A}'\mathbf{A}\mathbf{\hat{x}} = 0
\] 

The second equation in (5.5) gives the “normal” equations, which are represented in matrix form as:

\[
\mathbf{\hat{x}} = (\mathbf{A}'\mathbf{A})^{-1}\mathbf{A}'\mathbf{\hat{y}}.
\]

Here, \( \mathbf{B} = (\mathbf{A}'\mathbf{A})^{-1} \) is the “normal” matrix.

The normal equations form the procedural backbone of the fit. The change in the parameters from one fit iteration to the next are calculated according to

\[
\Delta \mathbf{x} = \mathbf{B}^{-1}\mathbf{A}'\Delta \mathbf{y},
\]

where

\[
\Delta \mathbf{x} = \mathbf{x}^{(n)} - \mathbf{x}^{(n-1)},
\]

is a column vector whose entries represent the change in each fit parameter from the previous iteration, and

\[
\Delta \mathbf{y} = \mathbf{y}^{(obs)} - \mathbf{y}^{(calc)}
\]

is a column vector representing the change in residuals.

When the change in each fit parameter becomes smaller than a specified tolerance, that parameter is said to be “converged”. The standard error of each fit parameter is then calculated according to
\[ \delta x_i = \sigma \left( B_i^{-1} \right)^{1/2}, \]  

(5.10)

where \( B_i \) represents the value of the \( i \)th diagonal element of the normal matrix as calculated following convergence. The relative uncertainty in parameter \( i \) is calculated from the standard error according to

\[ u_i = \frac{\delta x_i}{x_i}. \]  

(5.11)

Finally, the correlation coefficients, which indicate how strongly correlated the fit parameters may be calculated according to

\[ C_y = \frac{B_{y}^{-1}}{(B_{y}^{-1}B_{x}^{-1})}. \]  

(5.12)

If two variables are perfectly correlated, \( C_y \rightarrow \pm 1 \), and if they are perfectly uncorrelated, \( C_y \rightarrow 0 \). Each fit parameter is by definition perfectly correlated with itself; i.e. \( C_i = 1 \). The correlation coefficients provide a significant amount of useful diagnostic information on the resulting fit parameters. Strong correlation between two fit parameters typically indicates that (i) the parameters cannot be separably and/or reliably determined from the fit, because of errors in the model, errors in the data set, or because the data lacks sufficient sensitivity, or (ii) the two variables are “naturally” interrelated for some (perhaps unknown) theoretical reason.

### 5.3 Fit Procedure

The quantum defect fit was initialized using the \( \left. \mu_{i;i}^{(N)} \right|_{k^*} \) and \( \frac{\partial \mu_{i;i}^{(N)}}{\partial R} \) parameters determined previously in [5]. While initially these constants represented the energy level structure of the high \( (n^* > 10) \) Rydberg states
quite well, the initial agreement between the calculated levels and their observed positions was not as good for the lower Rydberg states. Systematic adjustment of these 40 fit parameters improved the agreement somewhat, but it soon became apparent that it was simply not possible to fit such an expansive data set using $\mu^{(\lambda)}_{\kappa}$ and $\frac{\partial \mu^{(\lambda)}_{\kappa}}{\partial R}$: the quantum defect model was in need of expansion. A strategy was therefore developed whereby the minimum number of necessary adjustable parameters could be added to the model, while at the same time maintaining confidence that the fitted constants maintain physically reasonable values. The procedure consisted of five main steps: (i) initialization and convergence using $\mu$ and $\frac{\partial \mu}{\partial R}$ parameters determined in reference [5], which compare well with ab initio estimates, (ii) division of the fit and subsequent convergence of each half, to determine estimates for $\frac{\partial \mu}{\partial E}$, (iii) convergence of fit using $\mu$, $\frac{\partial \mu}{\partial R}$, and $\frac{\partial \mu}{\partial E}$ parameters, and (iv) addition of any necessary quadratic derivatives; i.e. $\frac{\partial^2 \mu}{\partial R^2}$, $\frac{\partial^2 \mu}{\partial E^2}$, and $\frac{\partial^2 \mu}{\partial E \partial R}$.

(i) **Initialization and convergence using $\mu^{(\lambda)}_{\kappa}$ and $\frac{\partial \mu^{(\lambda)}_{\kappa}}{\partial R}$.**

The first step of the procedure is to fit the entire spectrum of energy levels starting with the $\mu^{(\lambda)}_{\kappa}$ and $\frac{\partial \mu^{(\lambda)}_{\kappa}}{\partial R}$ parameters determined in [5]. While it was apparent that this limited set of fit parameters would never allow perfect correspondence between the quantum defect model and the experimental data, some refinement of the parameters was expected (especially for the $\frac{\partial \mu^{(\lambda)}_{\kappa}}{\partial R}$ parameters) since the levels in the expanded data
set cover a wider range of \( v \) and participate in a greater number of vibronic perturbations, which should afford greater sensitivity to the dependence of the quantum defects on \( R \).

The refinement procedure itself was partially combinatorial. Initially, each \( \mu_{i\ell}^{(\Lambda)}|_{R'} \) and \( \frac{\partial \mu_{i\ell}^{(\Lambda)}}{\partial R} \) parameter was varied, \textit{one at a time}, to highlight those parameters whose values were in particular need of refinement. When a parameter was found that was poorly-fit, and when subsequent adjustment of this parameter significantly improved the fit quality, it was allowed to vary and its optimum value was taken for use in the next fit iteration.

Generally, the adjustment of matrix elements that are diagonal in \( \ell \) had the greatest impact on the fit quality. This process was repeated until it was not possible to improve the quality of the fit by adjusting the value of a single fit parameter. The procedure was then repeated using combinations of parameters, typically:

a) One \( \mu_{i\ell}^{(\Lambda)}|_{R'} \) parameter and its associated \( R \)-derivative

b) Two different diagonal \( \mu_{i\ell}^{(\Lambda)}|_{R'} \) parameters with the same value of \( \Lambda \),

c) Two different diagonal \( \mu_{i\ell}^{(\Lambda)}|_{R'} \) parameters with the same value of \( \Lambda \) as well as the off-diagonal matrix element between them; i.e. \( \mu_{\lambda\mu}^{(S)}|_{R'} \),

\[
\mu_{pp}^{(S)}|_{R'}, \text{ and } \mu_{pp}^{(S)}|_{R'},
\]

d) Combinations of parameters as in c), plus their \( R \)-derivatives

e) All \( \mu_{i\ell}^{(\Lambda)}|_{R'} \) matrix elements for a given \( \Lambda \), and

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f) All $\mu_{i,c}^{(\Lambda)} \big|_{R_c}$ and $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial R}$ matrix elements with a given $\Lambda$.

As stated earlier, strong attempts were made to adjust as few parameters as possible, and to ensure that this condition was met we typically attempted to vary 5 to 20 combinations of parameters at each step.

(ii) Generation of estimates of $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial E}$.

After the initial fit parameters were refined to convergence, according to the procedure described in (i), it became apparent that the energy dependence of the quantum defects would need to be considered as well. To generate estimates of the derivatives of the quantum defects with respect to energy, $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial E}$, the fit was divided into two halves: states with $n^* = 5 - 10$ in the first (“low energy”) half, and states with $n^* = 10 - 22$ in the second (“high energy”) half. Each half was then subject to the procedure described in section (i). This generated two sets of converged fit constants, from which estimates of each $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial E}$ could be obtained by linearization.

(iii) Convergence using $\mu_{i,c}^{(\Lambda)} \big|_{R_c}$, $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial R}$, and $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial E}$.

After estimates were obtained for the energy derivatives $\frac{\partial \mu_{i,c}^{(\Lambda)}}{\partial E}$ according to (ii), the data were again subject to an iterative fit procedure similar to steps (a)-(f) in (i). In this stage of the fit procedure, the energy derivatives were varied as well as the $R$-derivatives, and as before, new values for the fit parameters were selected by adjusting the most effective
combinations of the least number of fit parameters, until all parameters were fully converged.

(iv) **Refinement by addition of quadratic derivatives:**

\[
\frac{\partial^2 \mu_{i'i'}^{(\lambda)}}{\partial R^2}, \quad \frac{\partial^2 \mu_{i'i'}^{(\lambda)}}{\partial E^2}, \quad \text{and} \quad \frac{\partial^2 \mu_{i'i'}^{(\lambda)}}{\partial E \partial R}.
\]

Following the convergence of the fit in step (iii), quadratic \(\frac{\partial^2 \mu_{i'i'}^{(\lambda)}}{\partial R^2}\), \(\frac{\partial^2 \mu_{i'i'}^{(\lambda)}}{\partial E^2}\), and \(\frac{\partial^2 \mu_{i'i'}^{(\lambda)}}{\partial E \partial R}\) derivatives were added to improve the fit quality for the very lowest \((n^* \approx 5)\) Rydberg states. Quadratic parameters were adjusted, one at a time, to identify those parameters which would be most effective in improving the quality of the fit. As it was not possible to generate reliable estimates of the values of the quadratic derivatives, each parameter was adjusted with its initial value taken to be zero. Following the identification of the most important quadratic derivatives, combinations of these parameters were adjusted in a scheme that similar to the procedure outlined in steps (a)-(f) of (i). Only select quadratic derivatives were introduced; for the most part, only diagonal elements for \(\Sigma\) and \(\Pi\) symmetry were added.

When all parameters had converged, the fit was considered complete, as the addition of more parameters would impart undue flexibility to the fit model and likely result in physically unrealistic values.

### 5.4 Quality of Fit

Reduced term value plots, comparing the observed energy levels against the predicted level positions calculated using the resulting fit constants, are shown in Figures 5-1 through 5-4. Energy levels with low \(n^*\)
(less than approximately 10) generally fit to within 0.1-1.0 cm\(^{-1}\), while energy levels at high \(n^*\) fit to within 0.2 cm\(^{-1}\) as expected.

![Figure 5-1: Reduced term value plot comparing observed and calculated energy levels. This figure illustrates the typical fit quality observed at low \(n^*\).](image-url)
Figure 5-2: Reduced term value plot comparing observed and calculated energy levels. This figure illustrates the typical fit quality observed at low $n^*$. 
Figure 5-3: Reduced term value plot comparing observed and calculated energy levels. This figure illustrates the typical fit quality at high $n^*$. 
Figure 5-4: Reduced term value plot comparing observed and calculated energy levels. This figure illustrates the typical fit quality at high \( n^* \).

5.5 Quantum Defect Matrices of CaF

Before discussing the parameters that result from the fit, it is instructive to calculate just how large each of the parameters must be to have a measurable impact on the energy levels that are represented in our data set. Since the data set represents Rydberg states with \( v \) between 0 and 5, it is reasonable to take the endpoints of, say, the \( v=3 \) wavefunction as reasonable indicators of our range of sensitivity of the quantum defects over \( R \). The turning points of the \( v = 3 \) vibrational wavefunction are separated by approximately 0.5 \( a_0 \). Since the data set represents Rydberg states with
$n^*$ between 5 and 22, and the distance between $v = 5$ and the ionization threshold is approximately 4400 cm$^{-1}$, our data set covers about 0.04 Rydbergs of energy. A change in quantum defect of 0.02 constitutes a reasonable criterion for sensitivity. That is, if the addition or modification of a parameter caused a change in the quantum defect of 0.02 over our range of $E$ or $R$, it would not go unnoticed. The change required to bring about such a change in quantum defect is listed for each type of quantum defect parameter in Table 5-1.

<table>
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<tr>
<th>Order in R</th>
<th>Order in E</th>
<th>Value</th>
</tr>
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<td>0.02</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
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<td>1</td>
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<td>0</td>
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<td>12.50</td>
</tr>
<tr>
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<td>1</td>
<td>1.00</td>
</tr>
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</table>

Table 5-1. Values of various quantum defect derivatives required to cause a change of 0.02 in the quantum defects over the ranges of energy and internuclear distance spanned by the current data set. The order of the derivative with respect to energy and/or internuclear distance is indicated; for example, an order of one indicates that the parameter is linear with respect to the indicated variable.

The final quantum defect matrix elements are shown in Tables 5-2 through 5-5, along with the quantum defect matrix elements determined in the previous fit, as well their values at the conclusion of each step of the fit. The variation in fit parameters, from one point to the next, is much as one would expect. As is evident from the Tables, the equilibrium values changed very little between any of the five points listed; typically the change was in the third decimal place. The linear $R$ derivatives, for the most part, changed relatively little and typically the change was in the second decimal
place. The linear $E$ derivatives appear for the first time at the third point, and many change significantly between the third and fourth points. However, it should be realized that the entries in the third column represent only estimates, whereas the entries in the fourth column represent converged values that were determined after hundreds of hours of computing time. The change between the fourth and fifth points is also not unreasonable; the largest changes are for the $f\Sigma$, $pp\Pi$, and $dd\Pi$ derivatives, which govern the energy level positions of the $0.36\ \Pi$ and $f\ \Sigma$ Rydberg series, the lowest members of which were invariably the worst-fit levels in the entire data set. Aside from these cases, the addition of quadratic ($\partial^2\mu/\partial E^2$, $\partial^2\mu/\partial R^2$, and $\partial^2\mu/\partial E\partial R$) derivatives did not alter the linear derivatives from their converged values in the fourth column in an unreasonable way. This is generally the situation illustrated in the Tables; while the fit improved significantly from each point to the next, the addition of new parameters generally allowed the data to fit better without significant variation in the already well-determined parameters, even though all matrix elements and derivatives are naturally highly correlated. This affords much confidence that the fitted values represent physically reasonable values; in terms of overall effect on the energy level structure, the equilibrium values should have the strongest effect, the linear derivatives should have the next-strongest effect, and finally the quadratic parameters should have the weakest effect on the energy levels. This largely appears to be mirrored in the data presented in Tables 5-2 to 5-4.
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<th>(iii)</th>
<th>(iv)</th>
<th>(v)</th>
<th>(ii)-(i)</th>
<th>(iii)-(ii)</th>
<th>(iv)-(iii)</th>
<th>(v)-(iv)</th>
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<td>0.0000</td>
<td>0.0000</td>
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Table 5-2: Equilibrium quantum defect matrix elements, shown at five different points during the course of the fit. (i): Initial constants from previous work [5]. (ii) Constants at the end of the first step. (iii) Constants at the end of the second step. (iv) Constants at the end of the third step. (v) Constants at the end of the fourth step. Notice that the parameters change very little from one step to the next.
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<th>(iv)</th>
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Table 5-3: Linear quantum defect $R$-derivatives, shown at five different points during the course of the fit. (i): Initial constants from previous work [5]. (ii) Constants at the end of the first step. (iii) Constants at the end of the second step. (iv) Constants at the end of the third step. (v) Constants at the end of the fourth step. Notice that most parameters change by less than 0.10 quantum defect units.
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| fd | $\Delta$ |           |      |       |       |      |           |      |           |          |
| ff | $\Phi$  |           |      |       |       |      |           |      |           |          |

**Table 5-4:** Linear quantum defect $E$-derivatives, shown at five different points during the course of the fit. (i): Initial constants from previous work [5]. (ii) Constants at the end of the first step. (iii) Constants at the end of the second step. (iv) Constants at the end of the third step. (v) Constants at the end of the fourth step.
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**Table 5-5:** Quadratic quantum defect derivatives, from the end of the final step of the fitting procedure. The third column shows the quadratic derivatives with respect to internuclear distance, the fourth shows the quadratic derivatives with respect to energy, and the final column shows the “mixed” derivatives (linear in energy and linear in internuclear distance; overall quadratic).
Finally, it is useful to compare the behavior of the quantum defects of CaF with the behavior of its “parent” atom, Ca\(^+\). As has been discussed previously [10], the structure of CaF is understandable within the framework of ligand field theory. The electronic states of the molecule are treated as states of the free metal ion, perturbed by the electric field of the ligand. The electronic states are therefore all derived largely from the structure of the Ca\(^+\) atom, and the energy dependence of the CaF quantum defects should bear at least some resemblance to the quantum defects of Ca\(^+\). As shown in Figures 5-5 and 5-6, the quantum defects of the \(ns\) and \(nd\) series of Ca\(^+\) change by approximately 0.03 units over the \(5 \leq n < \infty\) range, which implies energy derivatives on the order of 0.75 \text{ Ry}^{-1}. It is interesting to note that many of the quantum defect energy derivatives in CaF are close to this value, and most range between 0.25 and 1.00 \text{ Ry}^{-1}. The energy derivatives resulting from our fit therefore appear to have reasonable magnitudes, based on this comparison with Ca\(^+\).
Figure 5-5: Effective principal quantum numbers of Ca$^+$ Rydberg states. (a) The ns series. (b) The np series. Figures were produced using data from [11]. The data available on the np series is incomplete.
Figure 5-6: Effective principal quantum numbers of Ca$^+$ Rydberg states. (a) The nd series. (b) The nf series. Figures were produced using data from [11].
5.6 Bibliography


Chapter 6

Dynamics: Resonance Between Electronic and Rotational Motions in Diatomic Molecules

Knowledge of the complete set of quantum defects of CaF enables the prediction of entirely new phenomena. In this chapter, the quantum defect model of CaF is used to examine the interaction between electronic and rotational motions in the high Rydberg states of CaF. Specifically, the model predicts resonances between these two motions when their classical periods are integer multiples of one another, and these resonances can be explained in terms of simple classical ideas and electrostatic arguments. These observations are generalized to predict how molecules of arbitrary polarity will behave under similar circumstances.

6.1 Frequencies of Motion

A fundamental property of molecular Rydberg states, as discussed in Chapter 2, is the strong dependence of the timescale of electronic motion on the principal quantum number, \( n \). As one ascends a Rydberg series, the classical period of motion of the outer electron becomes progressively slower. At some point, electronic motion occurs on a timescale comparable to (and
eventually slower than) the vibration of the nuclei, and further along the Rydberg series the classical period of motion of the electron approaches and eventually exceeds the period of rotation of the molecule. The spectra of the Rydberg states change correspondingly, and no less dramatically. At low principal quantum numbers the energy levels of the molecule are arranged into well-isolated electronic states with relatively simple rotational and vibrational structures. However, as the principal quantum number increases, the entire notion of an “electronic state” becomes questionable, and perturbations between states become the rule rather than the exception.

Although the spectra of high Rydberg states are generally complicated, at least at first glance, the fact that Rydberg states can in many ways be understood in essentially classical terms suggests that that some underlying simplicity may yet be present. Here, this underlying classical simplicity will be drawn out by using quantum defect theory to examine properties of the molecular wavefunctions of successive members of the Rydberg series of CaF. The utility of an understanding of the underlying classical behavior of such a molecular system goes far beyond mere intellectual satisfaction: wavepackets, for example, recover precisely this type of classical motion, and any attempt to create them and understand or manipulate their behavior is predicated on an understanding of the qualitative types of motions that are possible and which energy levels must be coherently excited to induce them.

In this set of calculations, the vibration of the nuclei and all effects due to spin are neglected, thereby isolating the effects of the interaction of two specific types of motion: the orbital motion of the Rydberg electron and the rotation of the nuclei. There are therefore two limiting dynamical situations: one in which the motion of the electron is strongly correlated
with the rotational motion of the nuclei (Hund’s case (b)), and one in which the electron moves essentially independently of them (Hund’s case (d)).

As discussed in Chapter 2, in Hund’s case (b), the motion of the Rydberg electron is coupled to the internuclear axis of the molecule and its orbital angular momentum $\ell$ is 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 $N^r$ 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. 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 $N^r$, are approximately conserved.

The extent to which the angular momenta of the two particles are conserved therefore serves as an indicator of the extent of their interaction, and will be our primary diagnostic tool. By calculating the molecular wavefunctions and expanding them into a basis in which $\ell$ and $N^r$ are well-defined, energy levels for which there is a strong interaction between the motions of the two particles will be immediately identified. Simple formulae will then be used to connect the quantum numbers of these levels with the classical periods of motion of the electron and ion, and this will allow the generation of an understanding of the underlying classical dynamics of the system.
6.2 Computational Details

To understand the interaction between electronic and rotational motion in CaF, multichannel quantum defect theory is used to compute and examine the composition of the wavefunctions of individual Rydberg states. Electron spin is neglected and the nuclei are assumed to be fixed at the ion core equilibrium internuclear separation of $R_v^+ = 3.54$ au. These calculations use the short-range quantum defect matrices and ion core structural parameters determined empirically by Jungen and Roche [1]. In this chapter, the reaction matrix representation is used exclusively. The molecular wavefunctions $\Psi(E)$ are expressed as superpositions of fragmentation channel functions:

$$\Psi(E) = \sum_{\ell N^+} B_{\ell N^+}(E) \psi_{\ell N^+}(E). \quad (6.1)$$

Here, $B_{\ell N^+}(E)$ are channel mixing amplitudes and

$$\psi_{\ell N^+}(E) = f_\ell (v_{N^+}(E)) \Phi^{(N)}_{\ell N^+} \delta_{\ell N^+;\ell' N^+} - \sum_{\ell' N^+} g_{\ell'} (v_{N^+}(E)) K_{\ell N^+;\ell' N^+} \Phi^{(N)}_{\ell' N^+}. \quad (6.2)$$

are the fragmentation channel functions. $f_\ell$ and $g_{\ell'}$ are respectively the regular and irregular Coulomb functions, with the zero of energy defined as the rotational level of the free ion with rotational quantum number $N^+$.

$\Phi^{(N)}_{\ell N^+}$ represent the combined angular wavefunctions of the electron and ion core, and $K_{\ell N^+;\ell' N^+}$ are elements of the long-range reaction matrix, which are related to the short-range quantum defect matrix elements $\mu_{\ell'}^{(\Lambda)}$ through the frame transformation [2]

$$K_{\ell N^+;\ell' N^+} = \sum_{\Lambda} \langle N^+ | \Lambda \rangle \tan \pi \mu_{\ell'}^{(\Lambda)} \langle \Lambda | N^+ \rangle. \quad (6.3)$$
Energy levels are found by demanding that the wavefunction of each eigenstate vanish at infinite electron-ion separation, giving rise to a system of homogeneous equations:

\[
\begin{bmatrix} P(E) + K \end{bmatrix} B = 0. \tag{6.4}
\]

Here \(K\) is the long-range reaction matrix, \(B\) is a column vector of channel mixing amplitudes \(B_{\ell N^*}\), and \(P(E)\) is the phase matrix \([3]\),

\[
P(E) = \begin{pmatrix}
\tan \pi \nu_{N^*} (E) & 0 & 0 & 0 \\
0 & \tan \pi \nu_{N^*+1} (E) & 0 & 0 \\
0 & 0 & \tan \pi \nu_{N^*+2} (E) & 0 \\
0 & 0 & 0 & \ldots
\end{pmatrix} \tag{6.5}
\]

where the effective principal quantum number \(\nu_{N^*} (E)\) is defined as

\[
\nu_{N^*} (E) = \sqrt{\frac{\Re}{E_{N^*} - E}}. \tag{6.6}
\]

The system of equations (6.4) has a solution at each energy for which the determinant of the coefficient matrix vanishes:

\[
\begin{vmatrix} P(E) + K \end{vmatrix} = 0. \tag{6.7}
\]

Once the energy levels are known, the channel mixing amplitudes \(B_{\ell N^*}\) are obtained at each such energy by finding the eigenvector of the matrix \((P(E) + K)\) with eigenvalue equal to zero. To reveal the composition of the eigenstates, the wavefunctions are expanded again (as described in Chapter 3.6) in terms of a new set of channel functions \(\overline{\varphi}_{\ell N^*}\) and channel mixing amplitudes \(C_{\ell N^*}\):

\[
\Psi(E) = \sum_{\ell, N^*} C_{\ell N^*} (E) \overline{\varphi}_{\ell N^*} (E). \tag{6.8}
\]

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where the channel functions \( \bar{\nu}_{N^+} \) are given by
\[
\bar{\nu}_{N^+} = f_\ell (v_{N^+}(E)) \cos(\pi \mu_{N^+}) - g_\ell (v_{N^+}(E)) \sin(\pi \mu_{N^+}) \Phi_{N^+}^{(N)}.
\] (6.9)

The new channel mixing amplitudes \( C_{N^+} \) are related to the original channel mixing amplitudes \( B_{N^+} \) through
\[
C_{N^+} = B_{N^+} \sec(\pi \mu_{N^+}),
\] (6.10)
where \( \mu_{N^+} \) is defined through the relationship
\[
\tan(\pi \mu_{N^+}) = \frac{\sum B_{N^+,N^+} K_{N^+,N^+}}{B_{N^+}}.
\] (6.11)

The fractional characters of the wavefunctions, expressed in terms of \( \ell \) and \( N^+ \), are then calculated according to
\[
P_{\ell} = \sum_{N^+} C_{N^+}^2
\] (6.12)
and
\[
P_{N^+} = \sum_{\ell} C_{N^+}^2.
\] (6.13)

In this set of calculations, the energy is varied in steps of 0.01 cm\(^{-1}\) and wavefunctions are found at all energies for which bound states exist. The calculations are performed separately for each total angular momentum \( N \) and interactions among channels with orbital angular momentum in the range \( 0 \leq \ell \leq 3 \) are considered. The dimensions of the long-range reaction matrix are determined by the vector addition \( N = \ell + N^+ \) and parity \( (-1)^{\ell+N^+} \), which gives ten \( \ell, N^+ \) pairs with (+) Kronig symmetry and six \( \ell, N^+ \) pairs with (-) Kronig symmetry for each value of \( N \). Eigenstates were located with binding energies between 4400 and 12 cm\(^{-1}\), which correspond to the
expected locations of Rydberg states with effective principal quantum number between 5 and 100. The eigenvectors resulting from the calculations are arranged into Rydberg series using the $C_{\ell N}$ coefficients. From $n = 5$ to $n \approx 40$ (here $n$ indicates the $n^{th}$ member of a series), the character of consecutive series members varies slowly with $n$ and individual eigenvectors can be arranged into Rydberg series based on a slow change in character as expressed by the $C_{\ell N}$ coefficients. For $20 < n < 40$ almost all series are observed to have greater than 50\% character in one $\ell, N^+$ channel, and above $n \approx 40$ eigenvectors were arranged into series using dominant character as the assignment criterion.

6.3 Analogy Between QDT and Effective Hamiltonian Theory

In the following discussion, the behavior of the (-) Kronig symmetry series will be examined, as their behavior is generally simpler than that of the (+) Kronig symmetry Rydberg series owing to the smaller number (6 vs. 10) of interacting channels. Figures 6-1 through 6-4 show the composition of the ‘p’$^\Pi$, ‘d’$^\Pi$, ‘d’$^\Delta$, and ‘f’$^\Delta$ (-) Kronig symmetry series as a function of increasing $n$. Figures 6-1 and 6-2 show the composition of the three series in terms of $P_{N^+}$, and Figs. 6-3 and 6-4 show their composition in terms of $P_\ell$.

Below $n \approx 25$, the ‘p’ $^\Pi$ and ‘d’ $^\Pi$ series are both strongly p-d mixed. However, above $n \approx 25$ both the electron orbital angular momentum composition and the rotational composition of all three series changes dramatically; for the most part, $\ell$-mixing tends to be diminished and each
series tends toward amplitude localized primarily in one rotational \(N^+\) channel. This suggests a tendency toward a decoupling of electronic and rotational motions, and although this decoupling is never complete, there is nevertheless a general trend toward convergence of each series to a different rotational level of the ion core. For \(N = 3\), the six decoupled channels with (-) Kronig symmetry are \((\ell, N^+) = (1,3), (2,2), (2,4), (3,1), (3,3)\) and \((3,5)\). These electron/ion decoupled channels correspond exactly to the dominant compositions of the six (-) Kronig symmetry series at high \(\ell\); we observe one nearly pure p series with \(N^+ = 3\); two d series, one with \(N^+ = 2\) and one with \(N^+ = 4\), and three f series, one each with \(N^+ = 1\), 3, and 5.
Figure 6-1: Rotational compositions of the the (a) ‘p’Π and (b) ‘d’Π (-) Kronig symmetry series as a function of increasing \( n \). This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.
Figure 6-2: Rotational compositions of the the (a) ‘d’Δ and (b) ‘f’Δ (-) Kronig symmetry series as a function of increasing $n$. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.
Figure 6-3: Partial-\(\ell\) compositions of the (a) ‘p’\(\Pi\) and (b) ‘d’\(\Pi\) (-) Kronig symmetry series as a function of increasing \(n\). This figure includes work which has been submitted to *Molecular Physics* (Taylor & Francis) and which is currently in press.
Figure 6-4: Partial-$\ell$ compositions of the (a) ‘d’Δ and (b) ‘f’Δ (-) Kronig symmetry series as a function of increasing $n$. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.
The behavior of the rotating molecule at low \( N \) and very low \( n \) (less than 10) may be reasonably approximated by the behavior of the nonrotating molecule, which is entirely governed by electron/ion scattering processes at short range. All of the properties of the molecule in this limit are governed by the structure of the short-range reaction matrix:

\[
K_{i'c}^{(A)}(\lambda) = \tan \left( \pi \mu_{i'i'}^{(A)} \right).
\] (6.14)

If the molecule did not rotate, there would be no \( \ell \)-uncoupling, and the molecule would adhere strictly to Hund’s case (b) coupling. The composition of the resulting “pure electronic” Rydberg series would not change with the principal quantum number, \( n \). The composition of each Rydberg series would then be determined exactly by the eigenvectors of the short-range reaction matrix, whose components give the relative amplitudes of each orbital angular momentum partial wave \( \ell \) in the Rydberg orbitals of each series. The quantum defects of each Rydberg series would likewise be constant with \( n \), and would be determined exactly by the eigenvalues of \( K_{i'c}^{(A)} \). This can be demonstrated mathematically by examining the behavior of the homogeneous system (6.4) at low energy \( E \). The reaction matrix \( K \) in (6.4) is nondiagonal, and the phase matrix \( P(E) \) is diagonal with entries \( \tan \pi \nu_{N^*} \left( E \right) \). Far below the ionization threshold, the effective principal quantum numbers \( \nu_{N^*} \) in each channel are approximately the same, and so \( \tan \pi \nu_{N^*} \left( E \right) \approx \tan \pi \nu_{N^{*+1}} \left( E \right) \approx \tan \pi \nu_{N^{*+2}} \left( E \right) \), etc. Thus, the phase matrix becomes a multiple of the identity matrix:
\[
P(E) = \begin{pmatrix}
\tan \nu_{\nu} (E) & 0 & 0 & 0 \\
0 & \tan \nu_{\nu-1} (E) & 0 & 0 \\
0 & 0 & \tan \nu_{\nu+1} (E) & 0 \\
0 & 0 & 0 & \ldots
\end{pmatrix} \approx \begin{pmatrix}
\tan \nu (E) & 0 & 0 & 0 \\
0 & \tan \nu (E) & 0 & 0 \\
0 & 0 & \tan \nu (E) & 0 \\
0 & 0 & 0 & \ldots
\end{pmatrix},
\]

(6.15)

and the system of equations (6.4) reduces to a simple eigenvalue problem:

\[
K \cdot \mathbf{B} = -P(E) \cdot \mathbf{B} = -\tan (\nu(E)) \cdot \mathbf{B} = \tan (\mu_a) \cdot \mathbf{B} \tag{6.16}
\]

Thus, in this limit, the molecular eigenfunctions (determined by the column vectors \( \mathbf{B} \)) are given simply by the eigenvectors of \( K \), and the quantum defect \( \mu_a \) of each Rydberg series is given by the inverse tangent of the corresponding eigenvalue of \( K \), divided by \( \pi \). The compositions and quantum defects of the pure electronic Rydberg series of \( \text{CaF} \) are given in Table 6-1. These are exactly the \( \ell \) compositions and quantum defects observed at low \( n \) in our calculations.

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>%s</th>
<th>%p</th>
<th>%d</th>
<th>%f</th>
</tr>
</thead>
<tbody>
<tr>
<td>'s' ( \Sigma )</td>
<td>0.45</td>
<td>89</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>'p' ( \Sigma )</td>
<td>0.14</td>
<td>8</td>
<td>89</td>
<td>3</td>
</tr>
<tr>
<td>'d' ( \Sigma )</td>
<td>-0.18</td>
<td>0</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>'p' ( \Pi )</td>
<td>-0.06</td>
<td>3</td>
<td>2</td>
<td>61</td>
</tr>
<tr>
<td>'d' ( \Pi )</td>
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<td>60</td>
<td>38</td>
<td>2</td>
</tr>
<tr>
<td>'p' ( \Delta )</td>
<td>0.03</td>
<td>40</td>
<td>53</td>
<td>8</td>
</tr>
<tr>
<td>'p' ( \Phi )</td>
<td>-0.03</td>
<td>0</td>
<td>9</td>
<td>90</td>
</tr>
<tr>
<td>'d' ( \Delta )</td>
<td>-0.14</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>'p' ( \Delta )</td>
<td>0.03</td>
<td>4</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>'p' ( \Phi )</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6-1: Partial-\( \ell \) characters of Rydberg series of \( \text{CaF} \). The partial-\( \ell \) characters shown here differ from those shown in Table 2-1 because this set of calculations is based upon an earlier set of quantum defects. This figure includes work which has been submitted to *Molecular Physics* (Taylor & Francis) and which is currently in press.
As the principal quantum number $n$ increases and the rotational thresholds are approached, the behavior of the molecule changes dramatically, and this is reflected mathematically in the change in behavior of the system of equations. To illustrate the change in behavior of the system of equations, let us consider the simpler case of two interacting channels converging to two different rotational thresholds. The homogeneous linear system for this case is

$$
\begin{pmatrix}
\tan \pi v_{N^+}^N(E) + K_{N^+,O^N} & K_{N^+,O^{N^+}} \\
K_{O^{N^+},N^+} & \tan \pi v_{N^+}^{O^N}(E) + K_{O^{N^+},O^{N^+}}
\end{pmatrix}
\begin{pmatrix}
B_{O^N} \\
B_{O^{N^+}}
\end{pmatrix} = 0 \quad (6.17)
$$

and the criterion for the existence of an energy level is

$$\det\begin{pmatrix}
\tan \pi v_{N^+}^N(E) + K_{N^+,O^N} & K_{N^+,O^{N^+}} \\
K_{O^{N^+},N^+} & \tan \pi v_{N^+}^{O^N}(E) + K_{O^{N^+},O^{N^+}}
\end{pmatrix} = 0. \quad (6.18)
$$

Near the ionization limits $\tan \pi v_{N^+}^N(E)$ will in general be quite different from $\tan \pi v_{N^+}^{O^N}(E)$, and so the system of equations does not reduce simply to the form of (6.16). Expansion of the determinant in (6.18) gives

$$\left(\tan \pi v_{N^+}^N(E) + K_{N^+,O^N}\right)\left(\tan \pi v_{N^+}^{O^N}(E) + K_{O^{N^+},O^{N^+}}\right) - K_{N^+,O^{N^+}}K_{O^{N^+},O^N} = 0. \quad (6.19)$$

Let us for the moment ignore the off-diagonal matrix elements $K_{N^+,O^{N^+}}$ and $K_{O^{N^+},O^N}$. The determinant then reduces to

$$\left(\tan \pi v_{N^+}^N(E) + K_{N^+,O^N}\right)\left(\tan \pi v_{N^+}^{O^N}(E) + K_{O^{N^+},O^{N^+}}\right) = 0, \quad (6.20)$$

implying that either $\tan \pi v_{N^+}^N(E) + K_{N^+,O^N} = 0$ or $\tan \pi v_{N^+}^{O^N}(E) + K_{O^{N^+},O^{N^+}} = 0$.

Thus, there would be energy levels at each energy for which $\tan \pi v_{N^+}^N(E) = -K_{N^+,O^N}$ or $\tan \pi v_{N^+}^{O^N}(E) = -K_{O^{N^+},O^{N^+}}$. We would therefore have Rydberg series with well-defined $\ell$ and $N^+$, converging to specific ionization.
thresholds, with quantum defects given by $\mu_{\text{mag}} = \frac{1}{\pi} \arctan(K_{G^*,0N^*})$ [4-5]. The molecule would therefore be in the Hund’s case (d) limit. Introduction of the off-diagonal matrix elements $K_{G^*,G'}$ and $K_{E^*,G'}$ would then produce perturbations between these two decoupled Rydberg series, and the strength of the perturbations would be determined entirely by the magnitude of the off-diagonal matrix elements and the energetic proximity of the two nearly-coincident zero-order energy levels (see Fig. 6-5).
Figure 6-5: Schematic energy level diagram showing zero-order energy levels and expected locations of strong resonance zones. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.

This picture establishes a clear analogy between quantum defect theory and the traditional effective Hamiltonian approach. From the point of view of an effective Hamiltonian, the electrostatic interactions between the electron and ion will generally give rise to matrix elements between case
(d) basis states that are both diagonal and off-diagonal in $\ell$ and $N^+$. If there were no off-diagonal matrix elements, $\ell$ and $N^+$ would always be good quantum numbers and each Rydberg series would have a constant quantum defect determined by the diagonal elements of the Hamiltonian. Introduction of the off-diagonal matrix elements then gives rise to perturbations between these Rydberg series. From the point of view of quantum defect theory, if the molecular Hamiltonian were diagonal in $\ell$ and $N^+$, the reaction matrix $K$ would also be diagonal in $\ell$ and $N^+$ and there would be no interactions between channels. The resulting Rydberg series would likewise have well-defined $\ell$ and $N^+$ and constant quantum defects determined by the diagonal elements of the $K$ matrix,

$$\mu_{(\ell N,)} = \pi^{-1} \arctan(K_{(\ell N,),(\ell N,)}).$$

Introduction of the off-diagonal matrix elements of $K$ then gives rise to interactions between channels, resulting in channel mixing (mixing of $\ell$ and $N^+$) and energy level shifts (deviations of the observed quantum defects, $\bar{\mu}_{(\ell N,)}$, from their unperturbed values,

$$\bar{\mu}_{(\ell N,)} = \pi^{-1} \arctan(K_{(\ell N,),(\ell N,)}).$$

When the energy levels associated with different channels become nearly degenerate, the effects of the channel interactions are strong; where the interacting levels are widely spaced, the effects are weak.

The results of the calculations illustrate this nicely. Figure 6-6 shows plots of the observed quantum defects $\bar{\mu}_{(\ell N,)}$ of two of the three core-penetrating (-) Kronig symmetry series. Comparing Figure 6-6 with Figures 6-1 through 6-4, it is clear that when the channel interactions are locally weak (as they are near $n = 35, 50,$ and $60,$ for example) each of the series have reasonably well-defined $\ell$ and $N^+$ quantum numbers and quantum
defects $\tilde{\mu}_{\ell N'}$ that are nearly equal to $\pi^{-1}\arctan\left(K_{\ell N',\ell N'}\right)$. Where the channel interactions are strong, each series has significant amplitude in several $\ell, N'$ channels and the quantum defects deviate from their unperturbed values. The oscillations in the quantum defects and in the channel mixing amplitudes shown in Figs. 6-1 through 6-4 are caused by resonances between electronic and rotational motion, and we will return to discuss these resonances in Chapter 6.4.
Figure 6-6: Effective quantum defects of (a) the 'p'II and (b) the 'd'II Rydberg series of CaF. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.
The evolution of the Rydberg series with increasing rotational excitation (total angular momentum $N$) is shown in Fig. 6-4. Figure 6-7(a) shows the rotational composition of the ‘p’ II series for $N = 10$ and Figure 6.7(b) shows the rotational composition of the same series for $N = 20$. As the figures illustrate, the main consequence of increasing the total angular momentum is a shift of the resonance locations to lower $n$; for example, at $N = 3$ the first resonance occurs at $n \approx 45$, whereas for $N = 10$ the first resonance occurs at $n \approx 30$. This can be understood quite simply in terms of the energy level diagram in Figure 6-2. As the total angular momentum $N$ increases, the rotational quantum numbers $N^r$ of the interacting channels correspondingly increase. The rotational thresholds then progressively separate, and levels with increasingly lower $n$ become systematically degenerate.
Figure 6-7: The rotational composition of the ‘p’ Π Rydberg series for (a) \( N=10 \) and (b) \( N=20 \). This figure includes work which has been submitted to *Molecular Physics* (Taylor & Francis) and which is currently in press.
6.4 Resonance Between Electronic and Rotational Motions

6.4.1 Kepler-Rotation Resonance

The discussion returns now to the channel interactions that occur for the (-) Kronig symmetry series, which are manifest with striking regularity in both the channel mixing amplitudes and quantum defect curves in Figures 6-1, 6-2, 6-3, 6-4, and 6-6. The oscillations that occur at \( n = 45, 55, 65, \) etc. in the figures are examples of “stroboscopic” resonances [6-7] and correspond to a resonance between the Kepler motion of the Rydberg electron and the rotational motion of the ion core. These resonances occur [6-9] when the classical period of Kepler motion of the Rydberg electron,

\[
\tau_{\text{Kepler}} = 2\pi n^3 \text{ [a.u.],}
\]

is equal to an integer multiple of the classical period of rotation of the ion core,

\[
\tau_{\text{Rot}} = \pi / B^+ \sqrt{N^+ (N^++1)} \text{ [a.u.],}
\]

where \( B^+ \) is the rotational constant of the ion (expressed in atomic units). Indeed, the period of rotation for \( N^+ = 3 \) (the average value of \( N^+ \) for the series with \( N = 3 \) shown in Figure 6-1) is approximately 13 picoseconds, and the Kepler periods for \( n = 45, 55, \) and 65 are approximately 13, 26, and 39 picoseconds, respectively. The first few resonances of this type are clearly visible in Figures 6-1 through 6-4, and are explicitly labeled in Figure 6-8 below. However, as the principal quantum number increases (for example, beyond approximately 70 for the series in Figure 6-1), the higher-order
resonances become overlapped and become difficult to disentangle from one another. The statement that the period of Kepler motion is equal to a multiple of the period of ion core rotational motion simply means that the energy levels associated with different rotational thresholds become degenerate across a reasonable range of energy (see Fig. 6-2); that is, the condition

$$E_{N^+,m_n} - E_{N^+,m_{n-1}} \approx E_{N^+,m_{n+m}} - E_{N^+,m_{n+m-1}},$$

(6.23)

with \( m \) integer, must be satisfied for several consecutive values of \( n \). When the energy levels become systematically degenerate in this way, the interactions between them lead to the formation of a strong resonance. When the resonance condition is not satisfied, there is little mixing of the wavefunctions and the energy levels are only weakly shifted.
Figure 6-8: Rotational compositions of the (a) 'p' II and (b) 'd' II Rydberg series for $N = 3$, with resonance zones highlighted. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.

The physical picture underlying the stroboscopic effect is that when the periods of electronic and rotational motion are equal, the electron strikes the ion core in the same rotational orientation upon each collision (or “lights
the core like a stroboscope” [6]). This interpretation has been confirmed both experimentally and theoretically [6-9]. The coupling between the Rydberg electron and the ion core becomes strong, the system effectively regains cylindrical symmetry, and in fact the molecule returns to case (b) coupling. This is shown in the cartoon diagram in Figure 6-9.

![Cartoon Diagram](image)

**Figure 6-9:** Cartoon diagram showing the rotational orientation of the ion core in the nonresonant case (left) and the resonant case (right).

Interestingly, in homonuclear molecules, such as Na₂, stroboscopic resonances occur whenever the Kepler period is a half-integer multiple of the rotational period of the ion core [6]. This is in fact a consequence of molecular symmetry: a half-rotation of the ion core of a homonuclear molecule is indistinguishable from a full rotation of the same core (see Fig. 6-10). At resonance, then, the outcome of each collision is the same whether the core has undergone any number of full rotations or any number of half-rotations. In CaF, however, we predict stroboscopic resonances to occur only when the Kepler period is an integer multiple of the rotational period of the ion core. Clearly, a half-rotation of a strongly polar heteronuclear ion such as CaF⁺ is not equivalent to a full rotation, so intuitively one would
expect that stroboscopic resonances should only occur when \( \tau_{\text{Kepler}} = n \cdot \tau_{\text{Rot}} \)
and that a qualitatively different physical picture should apply to CaF.

![Diagram showing CaF and Homonuclear molecules](image)

**Figure 6-10:** Cartoon illustrating the difference between Kepler-rotation resonances in heteronuclear (left) and homonuclear molecules (right).

The formation of stroboscopic resonances when

\[
\tau_{\text{Kepler}} = \frac{1}{2} \cdot \tau_{\text{Rot}}, \quad \frac{3}{2} \cdot \tau_{\text{Rot}}, \quad \frac{5}{2} \cdot \tau_{\text{Rot}}, \ldots
\]

in homonuclear molecules and their absence in CaF is not only borne out in the energy level patterns, but is in fact entirely a consequence of electrostatics. In Figure 6-11 the expected locations of energy levels associated with the three channels \((\ell, \, N^+)\), \((\ell^+, \, N^+ + 1)\) and \((\ell^-, \, N^+ + 2)\) are plotted roughly to scale. It is immediately apparent that the energy levels associated with channels differing by two quanta of rotation become systematically degenerate *twice* as often as those differing by *one* quantum of rotation. Furthermore, the systematic degeneracies that occur only in the \( \Delta N^+ = 2 \) case occur exactly at those values of \( n \) for which the Kepler period is a half-integer multiple of the rotational period. In a homonuclear molecule, inversion symmetry ensures that only even-rank electrostatic interactions between the electron and ion are possible, which
act exclusively between channels which differ in \( \ell \) by an even number (for example, s–d interactions). To conserve parity, these interactions must also act exclusively between channels which differ in \( N^t \) by an even number. Thus, the symmetry of a homonuclear molecule ensures that channel interactions of the type illustrated in Figure 6-11(b) occur, and ensures that channel interactions of the type illustrated in Figure 6-11(a) do not occur. CaF, on the other hand, possesses no center of symmetry and both even-rank and odd-rank interactions are possible. While interactions between all channels are in principle allowed, the even-rank electrostatic interactions in CaF are evidently so weak (see Table 6-1) that the only interactions of any

![Diagram of Energy and Interactions](image)

**Figure 6-11:** Comparison of channel interactions in nonpolar and strongly polar molecules. This figure includes work which has been submitted to *Molecular Physics* (Taylor & Francis) and which is currently in press.
consequence are between channels for which \( N^+ \) differs by an odd number, as in Figure 6-8(a). Consequently, exactly half as many stroboscopic resonances form for CaF as for a homonuclear molecule. The formation of twice as many Kepler-rotation resonances in homonuclear molecules is thus a result of both the nonsphericity and symmetry of the ion core, whereas the formation of only half as many in CaF is a result of the nonsphericity and polarity of the ion core.

It is straightforward to demonstrate how the stroboscopic resonances arise mathematically using the simplified two-channel problem discussed in Chapter 6.3. There, the criterion for the existence of an energy level was

\[
\det \begin{pmatrix}
\tan \pi v_{N^+} (E) + K_{\hat{N}^+, \hat{N}^+} & K_{\hat{N}^+, \hat{N}^+} \\
K_{\hat{N}^+, \hat{N}^+} & \tan \pi v_{N^+} (E) + K_{\hat{N}^+, \hat{N}^+}
\end{pmatrix} = 0.
\]

(6.24)

The resonance condition indicates that when there is a stroboscopic resonance between electronic and rotational motion, \( v_{N^+} = v_{N^+} \pm m \), with \( m \) integer. Thus, \( \tan \left( \pi v_{N^+} (E) \pm m \right) = \tan \pi v_{N^+} (E) \), and since

\[
\tan \left( \pi v_{N^+} (E) \pm m \right) = \tan \pi v_{N^+} (E), \quad \tan \pi v_{N^+} (E) = \tan \pi v_{N^+} (E).
\]

The phase matrix \( P(E) \) then becomes a multiple of the unit matrix:

\[
P(E) = \begin{pmatrix}
\tan \pi v_{N^+} (E) & 0 \\
0 & \tan \pi v_{N^+} (E)
\end{pmatrix} = \tan \pi v_{N^+} (E) \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\]

(6.25)

and the system (6.4) reduces to the eigenvalue equation

\[
K \cdot B = -P(E) \cdot B,
\]

(6.26)

just as in (6.16). Since the long-range reaction matrix that appears above in Eq. (6.26) is related to the short-range reaction matrix by a unitary transformation, its eigenvalues and eigenvectors are unchanged. Thus, at a stroboscopic resonance, the compositions and quantum defects of the
Rydberg series return to what they were at low $n$, and the molecule again follows case (b) behavior.

### 6.4.2 Precession-Rotation Resonance

If the destruction of the individual electron/ion angular momenta $\ell$ and $N^+$ is indicative of resonance between the motion of the two particles, which certainly is the case, then it should likewise be possible to describe the nature of the resonance that occurs near $n \approx 20$ for the $N = 3$ Rydberg series in Figure 6-12. At $n = 20$ the period of Kepler motion is only 1 ps, yet the period of rotational motion of the ion core (for $N^+ = 3$) is still 13 ps. Since these periods are not small-integer multiples of one another, this resonance must be qualitatively different than the Kepler-rotation resonances discussed in Chapter 6.4.1. To further illustrate the difference between the resonance at $n = 20$ and the stroboscopic resonances, in Figs. 6-13 and 6-14 are plotted the locations of the $N = 3$ unperturbed energy levels in the three strongly-interacting channels for both cases. Figure 6-13 shows the energy level patterns at the first stroboscopic resonance and Fig. 6-14 shows the energy level patterns in the vicinity of the $n = 20$ resonance. These two patterns are clearly distinct: whereas at the stroboscopic resonance energy levels differing in both $n$ and in $N^+$ and $\ell$ become degenerate (with $\Delta n = -\Delta N^+$), near $n = 20$ energy levels with the same value of $n$ but different values of $N^+$ and $\ell$ become degenerate. In both cases the degeneracy results from the equality of a difference in electronic energy and a difference in rotational energy, but whereas in the first case the difference in electronic energy is determined by the principal quantum number $n$, in the latter the difference
in electronic energy is determined solely by the quantum defects $\mu_{N^+}$. Just as the energy difference $E_{n+1} - E_n$ defines the frequency of radial (Kepler) motion of the electron and the difference $E_{N^{+1}} - E_{N^{+}}$ defines the frequency of rotational motion of the ion core, the difference $E_{n,\ell+1} - E_{n,\ell}$ defines the frequency of angular motion of the electron, or its frequency of precession.

![Diagram showing rotational composition of the 'd' Pi series, showing location of precession-rotation resonance. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.](image)

**Figure 6-12:** Rotational composition of the 'd' Pi series, showing location of precession-rotation resonance. This figure includes work which has been submitted to *Molecular Physics* (Taylor & Francis) and which is currently in press.
Figure 6-13: Scale diagram showing the zero-order energy level structure in the vicinity of the precession-rotation resonance. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.
Figure 6-14: Scale diagram showing the zero-order energy level structure in the vicinity of the first Kepler-rotation resonance. This figure includes work which has been submitted to Molecular Physics (Taylor & Francis) and which is currently in press.
In the classical Kepler problem, a bound particle in an attractive $\frac{1}{r}$ potential is confined to a planar elliptical orbit, as shown in Figure 6-15. In a pure $\frac{1}{r}$ potential, the period of inward/outward radial motion of the particle is exactly equal to its period of revolution about the force center, and the orbit is closed [10]. The addition of an isotropic perturbing potential of the form $r^{-k}$ to the attractive $\frac{1}{r}$ potential (the “perturbed” Kepler problem) disrupts the equality between the period of radial motion and the period of revolution and causes the orbit to precess, as shown in Figure 6-16. On average, the particle falls toward the center at a rate that is different than the rate at which it revolves about the center.

![Diagram showing vectors relevant to the pure Kepler problem.](image)

**Figure 6-15:** Diagram showing vectors relevant to the pure Kepler problem. $\mathbf{r}$ indicates the position vector, $\mathbf{p}$ indicates the momentum vector, $\mathbf{L}$ indicates the angular momentum vector, and $\mathbf{A}$ indicates the Runge-Lenz vector, which always points along the major axis of the orbit. This figure includes work which has been submitted to *Molecular Physics* (Taylor & Francis) and which is currently in press.
Analogous types of motion have been observed quantum-mechanically in wavepacket experiments and calculation involving alkali atoms. The excitation of a coherent superposition of Rydberg states of an alkali atom with identical $\ell$ but different $n$ creates a radial wavepacket that undergoes purely radial inward-outward motion [11-14]. The frequency of radial oscillation of the wavepacket is inversely proportional to the energy level spacing between states with different $n$. However, the excitation of a coherent superposition of Rydberg states with identical $n$ but different $\ell$ creates an angular wavepacket whose probability density revolves about the nucleus [15-18]. The frequency of angular motion of the wavepacket is
inversely proportional to the difference in energy between states with
different \( \ell \). That is, the angular motion of the wavepacket is governed by the
relative magnitudes of the quantum defects \( \mu \), and thus, in analogy to the
precessional motion in the classical perturbed Kepler problem, arises as a
result of the non-\( \frac{1}{r} \) potential felt by the outer electron.

The \( n = 20 \) resonance predicted here thus corresponds classically to a
resonance between the angular, or precessional, motion of the Rydberg
electron and the rotational motion of the ion core. In the case of one-
electron atoms it is the difference in quantum defects between the different
Rydberg series that determines the frequency of precessional motion. Here,
in CaF, it is the difference in quantum defect between two series that causes
the electronic energy difference to match the rotational energy difference. In
the atom, the core has no internal structure and the electron simply
undergoes angular motion. Here, the ion core can rotate, and the electron
can interact with this rotation; the electron now has something associated
with the ion core to resonate with.
6.5 Bibliography


Chapter 7

Mechanism: Physical Interpretation of Quantum Defect Parameters

This chapter describes ongoing work that seeks to understand the physical origins of the quantum defects of CaF and their dependences on the internuclear distance and the collision energy of the Rydberg electron. Central to this discussion is the separation of long-range and short-range interactions experienced by the Rydberg electron; this separation is accomplished using an extensively-modified version of the long-range model [1-10] in combination with numerous physical arguments. The weak penetration effects observed in the $nf$ Rydberg states are discussed, and the relative contributions of the long-range and short-range interactions to the quantum defects of the core-penetrating Rydberg series are assessed. The chapter concludes with a discussion of ligand field theory, and how it may be used to derive the quantum defect matrix of CaF and the dependence of each matrix element on $R$ and $E$.

7.1 Separation of Short-Range and Long-Range Interactions

The first step toward understanding the physical origins of the quantum defects of CaF is to separate the contributions from each of their
possible sources. The two main sources are (i) the long-range interactions between the electron and the ion; i.e. electric multipole and polarization interactions, and (ii) the short-range interactions between the electron and the ion; i.e. Coulomb and exchange between the Rydberg and core electrons [11]. These two effects can be separated through comparative study of the nonpenetrating and penetrating Rydberg states: while the structure of nonpenetrating states is almost entirely determined by the long-range interactions, the core-penetrating states are affected by both. If the strength of each of the long-range interactions can be determined using the nonpenetrating states, their effect on the penetrating Rydberg states can be predicted and subtracted. This leaves only the short-range portion, which can be analyzed separately.

7.1.1 The Basic Long-Range Model

The long-range model for nonpenetrating Rydberg states treats the nonpenetrating states of both atoms and molecules as hydrogenic eigenstates perturbed by long-range interactions with the ion core [1-5]. The effective Hamiltonian, for both atoms and nonrotating molecules, may be written as

$$\hat{H} = \hat{H}_{\text{Coulomb}} + \hat{H}_{\text{Core}} + \hat{H}_{el}^{(i)}. \quad (7.1)$$

Here $\hat{H}_{el}^{(i)}$ is the operator representing all non-Coulomb long-range interactions between the electron and ion, and includes perturbations by the permanent electric multipole fields of the ion core as well as polarization of the core electron orbitals by the Rydberg electron. The electric multipole interactions, which are typically much stronger than the polarization interactions, are of the general form [12]
\[ V(r, \theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sqrt{\frac{4\pi}{2\ell+1}} \frac{Y_{\ell m}(\theta, \phi)}{r^{\ell+1}} Q_{\ell m}, \]  

(7.2)

In a diatomic molecule, the cylindrical symmetry forces all terms with \( m \neq 0 \) to vanish, leaving

\[ V(r, \theta, \phi) = \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell+1} \frac{Y_{\ell 0}(\theta, \phi)}{r^{\ell+1}} Q_{\ell 0} = \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell+1} \frac{Y_{\ell 0}(\theta, \phi)}{r^{\ell+1}} Q_{\ell}, \]  

(7.3)

which may be written in terms of Legendre polynomials as

\[ V(r, \theta) = \sum_{\ell=0}^{\infty} \frac{Q_{\ell}}{r^{\ell+1}} P_{\ell}(\cos \theta). \]  

(7.4)

The \( \ell^{\text{th}} \) moment \( Q_{\ell} \) is defined as

\[ Q_{\ell} = \int dr' \rho(r')(r')^{\ell} P_{\ell}(\cos \theta) \]  

(7.5)

where \( \rho(r') \) is the charge density of the core at point \( r' \). Plots of the dipole, quadrupole, and octupole fields are shown in Figure 7-1. Matrix elements of the electric multipole operators in Eq. (7.4) are evaluated in a hydrogenic basis:

\[ \psi_{\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \]  

(7.6)

For diatomic molecules, the internuclear axis is taken as the axis of quantization, and the projection quantum number \( m \) is replaced by \( \lambda \).
The selection rules on the electric multipole operators of Eq. (7.4), summarized in Tables 7-1 and 7-2, are such that all odd multipole operators (dipole, $\ell = 1$; octupole, $\ell = 3$; etc.) have matrix elements that are exclusively off-diagonal in the orbital angular momentum quantum number $\ell$. On the other hand, the even multipole operators (quadrupole, $\ell = 2$; hexadecapole, $\ell = 4$; etc.) contribute matrix elements that are both diagonal and off-diagonal in $\ell$, and the off-diagonal matrix elements have a much weaker effect on the energy level structure. Now, in homonuclear molecules, all odd electric multipole moments vanish by symmetry and therefore only the even multipole operators need be considered. Because the dominant interactions are diagonal in both $\ell$ and $n$, the basis can usually be truncated to include only the set of $2\ell+1$ substates with common values of $\ell$ and $n$. For example, in NO (a near-homonuclear molecule) the $\Delta n \neq 0$ and $\Delta \ell \neq 0$ interactions are weak enough that the 4f states can be effectively treated as an isolated set of seven (4f$\Sigma^+$, 4f$\Pi^\pm$, 4f$\Delta^\pm$, and 4f$\Phi^\pm$) sublevels [11]. In heteronuclear diatomics, however, all electric multipole moments are in principle nonzero and the presence of the odd multipole fields can complicate
the analysis considerably, especially when one of the odd moments is large. The analysis is more complicated in this case because the \( \Delta n \neq 0 \) and \( \Delta \ell \neq 0 \) interactions cannot be neglected, and the basis must be expanded considerably.

<table>
<thead>
<tr>
<th>( \Delta \ell )</th>
<th>( r^{-2} )</th>
<th>( r^{-3} )</th>
<th>( r^{-4} )</th>
<th>( r^{-5} )</th>
<th>( r^{-6} )</th>
</tr>
</thead>
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<tr>
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<tr>
<td>( \pm 2 )</td>
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<td>o</td>
<td>o</td>
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<tr>
<td>( \pm 3 )</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
<td>( \pm 4 )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>o</td>
</tr>
</tbody>
</table>

Table 7-1: Selection rules on operators that form the radial portion of the electric multipole operators. “x” indicates that the operator has nonzero matrix elements for the specified value of \( \Delta \ell \) only when \( \Delta n \neq 0 \). “o” indicates that the operator has nonzero matrix elements for all values of \( \Delta n \).

<table>
<thead>
<tr>
<th>( \Delta \ell )</th>
<th>( P_1(\cos \theta) )</th>
<th>( P_2(\cos \theta) )</th>
<th>( P_3(\cos \theta) )</th>
<th>( P_4(\cos \theta) )</th>
</tr>
</thead>
<tbody>
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<tr>
<td>( \pm 1 )</td>
<td>o</td>
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<td>( \pm 2 )</td>
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<td>( \pm 3 )</td>
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<tr>
<td>( \pm 4 )</td>
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<td>-</td>
<td>o</td>
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</tbody>
</table>

Table 7-2: Selection rules on operators that form the angular portion of the electric multipole operators. “o” indicates that the operator has nonzero matrix elements for all values of \( \Delta n \). “-” indicate that all matrix elements are zero for the specified value of \( \Delta \ell \).

Watson [5] devised a way to cope with the presence of a large dipole moment using perturbation theory. Because the dipole operator has exclusively off-diagonal elements (selection rules \( \Delta n = \pm 1 \) and \( \Delta \ell = \pm 1 \)), the first-order correction to the energy levels in the perturbation expansion
\[ E_{n\ell\lambda} = E^{(0)}_{n\ell} + E^{(1)}_{n\ell\lambda} + E^{(2)}_{n\ell\lambda} + \ldots \]
\[ = E^{(0)}_{n\ell} + \langle \psi^{(0)}_{n\ell\lambda} | V(r) | \psi^{(0)}_{n\ell\lambda} \rangle + \sum_{n' \ell' \lambda'} \left| \frac{\langle \psi^{(0)}_{n'\ell'\lambda'} | V(r) | \psi^{(0)}_{n\ell\lambda} \rangle}{E^{(0)}_{n'\ell'} - E^{(0)}_{n\ell}} \right|^2 + \ldots \] (7.7)

vanishes. However, the second-order correction is nonzero and, according to Watson’s formalism, has the value
\[ E^{(2)}_{n\ell\lambda} = \mu^2 \frac{2 \left[ \ell (\ell + 1) - 3 \lambda^2 \right]}{n^3 (2\ell + 3)(2\ell + 1)(2\ell - 1) \ell (\ell + 1)}. \] (7.8)

The utility of Watson’s approach is that it allows the effects of an infinite number of interactions among an infinite number of energy levels to be calculated using a closed-form expression, and more importantly, no expansion of the basis (beyond the usual 2\ell+1 substates typically employed for homonuclear molecules) is necessary. Because it is a perturbative method, it is not exact, but the error is typically negligible and caution need only be exercised when \( \ell < 3 \) and \( \mu > 3 \) au.

For both homonuclear and heteronuclear molecules, evaluation of the matrix elements of even multipole operators is quite simple. The first-order diagonal matrix elements are [13-15]
\[ \langle \psi_{n\ell\lambda} | V_{\ell} (r) | \psi_{n\ell\lambda} \rangle = \langle R_{n\ell} | \frac{1}{r^{\ell+1}} | R_{n\ell} \rangle \sqrt{\frac{4\pi}{2\ell + 1}} \langle Y_{\ell\lambda} | Y_{\ell\lambda} | Y_{\ell\lambda} \rangle, \] (7.9)
\[ = \langle R_{n\ell} | \frac{1}{r^{\ell+1}} | R_{n\ell} \rangle \langle Y_{\ell\lambda} | C_q^k | Y_{\ell\lambda} \rangle, \]
in which
\[ \langle Y_{\ell\lambda} | C_q^k | Y_{\ell\lambda} \rangle = (-1)^{-\lambda} C^{\ell \lambda}_{k \ell \lambda q} \langle \ell || C(k) || \ell \rangle \] (7.10)
and the reduced matrix elements \( \langle \ell || C(k) || \ell \rangle \) are
\[ \langle \ell | C(k) | \ell \rangle = (-1)^\ell (2\ell + 1) \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}. \]  
(7.11)

The final matrix element for the first-order quadrupole interaction is

\[ \langle \psi_{n\ell 4} | V_{\ell=2} (r) | \psi_{n\ell 4} \rangle = \frac{Q}{n^3} \frac{2\left[ \ell (\ell + 1) - 3 \lambda^2 \right]}{(2\ell + 3)(2\ell + 1)(2\ell - 1)\ell(\ell + 1)}, \]  
(7.12)

and the final matrix element for the first-order hexadecapole interaction is

\[ \langle \psi_{n\ell 4} | V_{\ell=4} (r) | \psi_{n\ell 4} \rangle = H \frac{3\left[ 5n^2 - 3\ell (\ell + 1) + 1 \right] \left[ \ell (\ell + 1) - 2 \right]}{n^4 (\ell + 2)(\ell + \frac{3}{2})(\ell + 1)\ell(\ell - \frac{3}{2})(\ell - 1)} \times \left\{ 35\lambda^4 + 5\left[ 5 - 6\ell (\ell + 1) \right] \lambda^2 + 3\left[ \ell^2 (\ell + 1)^2 - 2\ell (\ell + 1) \right] \right\} \]  
(7.13)

The similarity between the first-order quadrupole matrix elements of Eq. (7.12) and the second-order dipole matrix elements of Eq. (7.8) is a general result: odd multipole operators operating in second order effectively behave as even multipole operators operating in first order.

Besides perturbations by the permanent electric multipole moments of the core, the polarization of the core by the Rydberg electron must also be considered [1, 2]. In lowest order, the polarization interactions give rise to a scalar term (the “isotropic polarization”, or “scalar dipole polarization” interaction) and a second-rank tensor term (the “anisotropic polarization”, or “tensor dipole polarization” interaction), which for cylindrically symmetric molecules have the forms

\[ V_{\text{oos}}^{(D)} (r) = -\frac{1}{2} \frac{\alpha}{r^4} \]  
(7.14)

and

\[ V_{\text{ooso}}^{(D)} (r, \theta) = -\frac{1}{3} \frac{1}{r^4} P_2(\cos \theta), \]  
(7.15)

and their matrix elements are
\begin{align}
\langle \Psi_{n\ell \lambda} | V^{(i)}_{\text{iso}} | \Psi_{n\ell \lambda} \rangle &= \alpha \frac{2 \left( \ell (\ell + 1) - 3 n^2 \right)}{n^3 (2\ell + 3)(2\ell + 1)(2\ell - 1) \ell (\ell + 1)} \tag{7.16}
\end{align}

and

\begin{align}
\langle \Psi_{n\ell \lambda} | V^{(i)}_{\text{aniso}} | \Psi_{n\ell \lambda} \rangle &= \gamma \frac{4 \left( \ell (\ell + 1) - 3 n^2 \right)}{3n^3 (2\ell + 3)^2 (2\ell + 1)(2\ell - 1)^2 \ell (\ell + 1)} \left\{ \ell (\ell + 1) - 3 \lambda^2 \right\} \tag{7.17}
\end{align}

The isotropic polarizability \( \alpha \) and anisotropic polarizability \( \gamma \) are defined in terms of the components of the polarizability tensor as

\begin{align}
\alpha &= \frac{2a_{\perp} + a_{\parallel}}{3} \tag{7.18}
\end{align}

and

\begin{align}
\gamma &= a_{\parallel} - a_{\perp} \tag{7.19}
\end{align}

in which \( a_{\parallel} = a_{zz} \) is the polarizability of the core along a direction parallel to the internuclear axis, and \( a_{\perp} = a_{xx} = a_{yy} \) is the polarizability of the core perpendicular to the internuclear axis.

So far we have only considered the electrostatic part of the Hamiltonian. To incorporate the effects of molecular rotation, we must augment the Hamiltonian of Eq. (7.1) to include the rotational Hamiltonian of the molecule:

\begin{align}
\hat{H} = \hat{H}_{\text{Coulomb}} + \hat{H}_{\text{el}} + \hat{H}_{\text{rot}} \tag{7.20}
\end{align}

Neglecting electron and nuclear spin, the pattern-forming rotational quantum number is \( N = J - S \), and the rotational Hamiltonian becomes [16]

\begin{align}
\hat{H}_{\text{rot}} &= B(R) \left[ N^2 + \ell^2 - 2N_{\ell z} \ell \cdot N^* \ell - N^* \ell \cdot N \ell^* \right]. \tag{7.21}
\end{align}

The first three terms in Eq. (7.21) are diagonal in \( N, \ell \), and \( \lambda \) with matrix elements

185
\[ \langle N\ell \lambda | \hat{H}_\text{rot} | N\ell \lambda \rangle = E^{(0)}_{\text{rot}} = B \left[ N(N+1) + \ell(\ell+1) - 2\lambda^2 \right], \tag{7.22} \]

while the fourth and fifth terms (the “\(\ell\)-uncoupling” operators) are diagonal in \(N\) and \(\ell\) but off-diagonal in \(\lambda\) (selection rule \(\Delta \lambda = \pm 1\)), with matrix elements:

\[ \langle N\ell \lambda | \hat{H}_\text{rot} | N\ell \lambda \pm 1 \rangle = -B(R) \sqrt{N(N+1) - \lambda(\lambda \pm 1)} \sqrt{\ell(\ell+1) - \lambda(\lambda \pm 1)} \cdot F. \tag{7.23} \]

Here, \(F\) is a symmetry factor arising from the degeneracy of \(\Lambda^+\) and \(\Lambda^-\) substates, and has the value \(F = \frac{1}{2}\) when \(\lambda = 0\) or \(\lambda' = 0\) and \(F = 1\) otherwise.

Watson [5] also notes that the electric dipole operator also has second-order effects on some matrix elements in the rotational Hamiltonian. In the absence of a dipole field, the matrix elements of \(\ell^2\), \(\ell^+\), and \(\ell^-\) are

\[ \langle \psi_{n\ell\lambda \pm 1} | \ell^2 | \psi_{n\ell\lambda} \rangle^{(0)} = \ell(\ell+1). \tag{7.24} \]
\[ \langle \psi_{n\ell\lambda \pm 1} | \ell^\pm | \psi_{n\ell\lambda} \rangle^{(0)} = \sqrt{\ell(\ell+1) - \lambda(\lambda \pm 1)}. \tag{7.25} \]

When the dipole moment is nonzero, an additional second-order contribution arises:

\[ \langle \psi_{n\ell\lambda \pm 1} | \ell^2 | \psi_{n\ell\lambda} \rangle^{(2)} = -\frac{\mu^2}{2\ell^2(\ell+1)^2} \ell(\ell+1), \tag{7.26} \]
\[ \langle \psi_{n\ell\lambda \pm 1} | \ell^\pm | \psi_{n\ell\lambda} \rangle^{(2)} = -\frac{\mu^2}{2\ell^2(\ell+1)^2} \sqrt{\ell(\ell+1) - \lambda(\lambda \pm 1)}, \tag{7.27} \]

and the matrix elements of \(\ell^2\), \(\ell^+\), and \(\ell^-\) therefore become

\[ \langle \psi_{n\ell\lambda \pm 1} | \ell^2 | \psi_{n\ell\lambda} \rangle = \left[ 1 - \frac{\mu^2}{2\ell^2(\ell+1)^2} \right] \ell(\ell+1). \tag{7.28} \]
\[ \langle \psi_{n\ell\lambda \pm 1} | \ell^\pm | \psi_{n\ell\lambda} \rangle = \left[ 1 - \frac{\mu^2}{2\ell^2(\ell+1)^2} \right] \sqrt{\ell(\ell+1) - \lambda(\lambda \pm 1)}. \tag{7.29} \]
The net effect of a nonzero dipole field is therefore to reduce the value of the matrix elements of $\ell^2$, $\ell^+$, and $\ell^-$ by an amount proportional to $\mu^2$. Watson refers to this effect as “orbit-rotation drag”, and its physical interpretation is that the dipole field reduces the rate of decoupling of $\ell$ from the internuclear axis. Classically, the core dipole exerts a “drag” force on the Rydberg electron, which opposes the Coriolis force caused by molecular rotation. Quantum-mechanically, the mixing of the orbital angular momentum $\ell$ is stronger for $\Delta \ell = -1$ than it is for $\Delta \ell = +1$, effectively reducing the value of $\ell$ to an effective noninteger value $\ell^* \prec \ell$.

### 7.1.2 The Extended Long-Range Model

A preliminary analysis of the nonpenetrating states identified in Chapter 4 indicated that the long-range model described above does not adequately describe the energy level structure of the $nf$ states of CaF. The long-range model has therefore been augmented to include the effects of higher-order multipole fields. Since CaF$^+$ is extremely polar, it is reasonable to expect that the higher-order electric multipole fields may have a measurable impact on the energy level structure, and preliminary calculations indeed indicated that the octupole field may give rise to as much as 5% d-f mixing. However, the matrix elements of the next highest polarization term, the adiabatic quadrupole polarization interaction,

$$V_{\text{red}}^{(Q)}(r, \theta) = -\frac{1}{r^6}\left(\frac{Z_0}{10} + \frac{Z_2}{7} P_2(\cos \theta) + \frac{12Z_4}{35} P_4(\cos \theta)\right)$$

(7.30)

should be weaker by a factor of at least 70 for 13f even if the magnitude of the adiabatic quadrupole polarizability were equal to the magnitude of the
adiabatic dipole polarizability. If this were the case, it would contribute energy level shifts that are significantly below our experimental sensitivity limit of ~0.05 cm\(^{-1}\). Attention will therefore be restricted to the higher-order permanent electric multipole operators.

To develop expressions for the matrix elements of the higher-order multipole interactions, it should first be noted that the second-order term in the perturbation expansion of Equation (7.7)

\[
E^{(2)}_{nl} = \sum_{n'l'} \left\langle \psi^{(0)}_{n'l'} | V(r) | \psi^{(0)}_{nl} \right\rangle^2 / (E^{(0)}_{n'l'} - E^{(0)}_{nl})
\]  

(7.31)

contains a square in the numerator, which will give rise to cross-terms between the terms in the electric multipole expansion

\[
V(r, \theta) = -\frac{\mu}{r^2} P_1(\cos \theta) - \frac{O}{r^3} P_3(\cos \theta) - \frac{O}{r^4} P_4(\cos \theta) - \frac{H}{r^5} P_5(\cos \theta) \ldots
\]  

(7.32)

Cross-terms between even and odd multipole moments vanish on account of parity, and the only cross-terms that remain are those with overall positive parity. The nonzero second-order cross-terms are:

\[
V_{11}(r, \theta) = \frac{\mu}{r^2} P_2(\cos \theta) \frac{\mu}{r^2} P_2(\cos \theta),
\]  

(7.33)

\[
V_{22}(r, \theta) = \frac{O}{r^3} P_3(\cos \theta) \frac{O}{r^3} P_3(\cos \theta),
\]  

(7.34)

\[
V_{33}(r, \theta) = \frac{O}{r^4} P_4(\cos \theta) \frac{O}{r^4} P_4(\cos \theta),
\]  

(7.35)

and

\[
V_{13}(r, \theta) = \frac{\mu}{r^2} P_2(\cos \theta) \frac{O}{r^4} P_4(\cos \theta).
\]  

(7.36)

In the above, the subscripts on \( V \) stand for \( \ell \) and \( \ell' \) respectively; for example, \( V_{13} \equiv V_{\ell=1, \ell'=3} \). The matrix elements in Equations (7.33)-(7.36)
represent the second-order dipole, second-order quadrupole, second-order octupole, and second-order dipole-octupole interactions.

The effective operator method developed by Kazansky and Ostrovsky [17, 18] is then used to calculate the matrix elements of these operators. In their method, the traditional perturbation sum in Eq. (7.7) is replaced by a Green’s function:

$$E_{n\ell\lambda} = E_{n\ell}^{(0)} + \langle \psi_{n\ell\lambda}^{(0)} \mid V \psi_{n\ell\lambda}^{(0)} \rangle + \langle \psi_{n\ell'\lambda}^{(0)} \mid V \tilde{G}(E) V \psi_{n\ell\lambda}^{(0)} \rangle + \ldots ,$$  \hspace{1cm} (7.37)

and the effect of the Green’s functions is expressed in terms of an effective tensor operator $\hat{W}$:

$$\langle \psi_{n'\ell'\lambda}^{(0)} \mid (A_{k_1} V_{k_1}) \tilde{G}(E) (A_{k_2} V_{k_2}) \psi_{n\ell\lambda}^{(0)} \rangle = \langle \psi_{n'\ell'\lambda}^{(0)} \mid \hat{W} \psi_{n\ell\lambda}^{(0)} \rangle ,$$  \hspace{1cm} (7.38)

Here, the $V_k$ represent the individual terms of the multipole expansion and the $A_k$ represent their coefficients, for example $A_2 V_2 = -\frac{Q}{r^3} P_2(\cos \theta)$, the quadrupole term. The operator $\hat{W}$ is itself a sum of $\ell+1$ tensor operators $\hat{W}_{q}^{k}$,

$$\hat{W} = \sum_{k,q} A_{kq} \hat{W}_{q}^{k} .$$  \hspace{1cm} (7.39)

Here the rank of the effective operator $\hat{W}_{q}^{k}$ is given by $k$, and the components of the tensor are indexed by $q$. The effective moment $A_{kq}$ of each effective tensor operator $\hat{W}_{q}^{k}$ is given by the tensor product of the coefficients of the electric multipole moment comprising the cross-term,

$$A_{kq} = (A_{s_1} \otimes A_{s_2})_{kq}$$  \hspace{1cm} (7.40)

in which
\[ (A_{\kappa_1} \otimes A_{\kappa_2})_{kq} = C^{i,q}_{\kappa_1, \kappa_2} \cdot (7.41) \]

Here, \( C^{q,i}_{\kappa_1, \kappa_2} \) is the Clebsch-Gordan coefficient \( \langle \kappa_1 q_1, \kappa_2 q_2 | \kappa_1, \kappa_2, k q \rangle \). The effective tensor operators \( W_{q^i} \) are expressed in terms of reduced matrix elements \( \langle \ell_1 \| W_k \| \ell_3 \rangle \), just as in Eq. (7.10):

\[ \langle \psi^{(0)}_{n^1 l^1 \lambda} \| W_{kq} \| \psi^{(0)}_{m^1 l^1 \lambda} \rangle = (-1)^{\ell_1 - \lambda_1} \begin{pmatrix} \ell_1 & k & \ell_2 \\ -\lambda_1 & q & \lambda_3 \end{pmatrix} \langle \ell_1 \| W_k \| \ell_3 \rangle . \quad (7.42) \]

The reduced matrix elements \( \langle \ell_1 \| W_k \| \ell_3 \rangle \) consist of products of radial and angular terms,

\[ \langle \ell_1 \| W_k \| \ell_3 \rangle = \sum_{\ell_2} \langle \ell_1 \| w^{(k)}_{\ell_2} \| \ell_3 \rangle \langle R_{m^1} \| v_{\kappa_1} \tilde{g}_{\ell_1} v_{\kappa_2} \| R_{m^3} \rangle , \quad (7.43) \]

and the angular portion is given by

\[ \langle \ell_1 \| w^{(k)}_{\ell_2} \| \ell_3 \rangle = (-1)^{\ell_2 \ell_1 + \ell_1 k} (2\ell_2 + 1) \sqrt{(2\ell_1 + 1)(2\ell_3 + 1)(2k + 1)} \times \begin{pmatrix} \ell_1 & \kappa_1 & \ell_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & \kappa_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \kappa_1 & \kappa_2 & k \\ \ell_3 & \ell_1 & \ell_2 \end{pmatrix} . \quad (7.44) \]

The radial matrix elements \( \langle R_{m^1} \| v_{\kappa_1} \tilde{g}_{\ell_1} v_{\kappa_2} \| R_{m^3} \rangle \) are expressed in terms of a reduced Green’s function \( \tilde{g}_{\ell_1} \), and may be generated by recursion.

The recursive generation of the matrix elements \( \langle R_{m^1} \| v_{\kappa_1} \tilde{g}_{\ell_1} v_{\kappa_2} \| R_{m^3} \rangle \) is based on the fact that the hydrogenic radial wavefunctions \( R_{m^1} (r) \) may be expressed in terms of spherical Bessel functions,

\[ R_{m^1} (r) = \frac{\sqrt{2}}{n^2} \frac{1}{\sqrt{r}} J_{2\ell_1 + 1} \left[ \frac{\sqrt{8r}}{n^2} \right] , \quad (7.45) \]

for which a recursion relationship exists. The recursion relation is

\[ \frac{1}{\sqrt{8r}} J_{2\ell_1 + 1} \left[ \sqrt{8r} \right] = \frac{1}{2(2\lambda + 1)} \left( J_{2\lambda} \left[ \sqrt{8r} \right] + J_{2\lambda + 2} \left[ \sqrt{8r} \right] \right) . \quad (7.46) \]

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Thus,
\[ \frac{1}{r} R_{nl} = \frac{1}{\sqrt{2}} \left( \frac{1}{\ell+\frac{1}{2}} \left( R_{n\ell-1} + R_{n\ell} \right) + \frac{1}{\sqrt{2}} \left( R_{n\ell} + R_{n\ell+1} \right) \right). \]  

(7.47)

Ostrovsky explicitly gives the effective second-order dipole radial matrix element as
\[ \langle R_{n\ell} \left| \frac{1}{r^2} \mathcal{G}_{\zeta_1} \frac{1}{r^2} \mathcal{G}_{\zeta_2} \right| R_{n\ell} \rangle = \frac{2}{\pi n^2} \frac{1}{(\ell - \ell_1)(\ell_1 + \ell_2 + 1)(\ell + \ell_1 + 1)} \times \left( \frac{(2\ell_1 + 1)^2 + (2\ell_2 + 1)^2 - 2(2\ell_1 + 1)^2}{4(\ell - \ell_2)(\ell + \ell_1 + 1)} \right) \sin \left[ \pi (\ell_1 - \ell_2) \right] - \sin \left[ \pi (\ell_1 + \ell_2 - 2\ell_1) \right]. \]  

(7.48)

Using this matrix element it is possible to generate matrix elements for any of the cross-terms in the multipole expansion. It should be noted that equation (7.48) has many removable singularities, and must be explicitly evaluated for all possible values of the three angular momenta. Limits must be taken when two of the angular momenta are equal, and it will generally be found that the appearance of \( \sin x / x \) functions remove the singularities under such circumstances. Equations (7.47) and (7.48) may be combined to give the recurrence relationship
\[ \langle R_{n\ell} \left| \frac{1}{r^{2\kappa-1}} \mathcal{G}_{\zeta_1} \frac{1}{r^{2\kappa-1}} \mathcal{G}_{\zeta_2} \right| R_{n\ell} \rangle = \left[ \langle R_{n\ell} \left| \hat{\mathcal{D}}_{\zeta_1}^{2\kappa-2} \right| R_{n\ell} \rangle \right] \left[ \langle R_{n\ell} \left| \frac{1}{r^{2\kappa-1}} \mathcal{G}_{\zeta_2} \frac{1}{r^{2\kappa-1}} \mathcal{G}_{\zeta_1} \hat{\mathcal{D}}_{\zeta_2}^{2\kappa-2} \right| R_{n\ell} \rangle \right]. \]  

(7.49)

Here, the operator \( \hat{\mathcal{D}}_\zeta \) acts \( 2\kappa-2 \) times on the left, and the operator \( \hat{\mathcal{D}}_\zeta \) acts \( 2\kappa-2 \) times on the right. The operators \( \hat{\mathcal{D}}_\zeta \) are defined through
\[ \hat{\mathcal{D}}_\zeta \left[ R_{n\ell} \right] = \frac{1}{\sqrt{2} (\ell + \frac{1}{2})} \left( R_{n\ell+\frac{1}{2}} + R_{n\ell-\frac{1}{2}} \right). \]  

(7.50)

The final contributions are, for the second-order dipole interaction, effective matrix elements of rank 0 and 2:
\[ \langle \psi_{n\ell\lambda} \left| V_{11} \right| \psi_{n\ell\lambda} \rangle^{(2,k=0)} = 0 \]  

(7.51)
\[ \langle \psi_{nl\ell} | V_{11} | \psi_{nl\ell} \rangle^{(2,k=2)} = \mu^2 \frac{2 \{ \ell (\ell + 1) - 3 \lambda^2 \}}{n^3 (2 \ell + 3)(2 \ell + 1)(2 \ell - 1) \ell (\ell + 1)}. \] (7.52)

The electric quadrupole moment in second order contributes matrix elements of rank 0, 2, and 4. The scalar term is

\[ \langle \psi_{nl\ell} | V_{22} | \psi_{nl\ell} \rangle^{(2,k=0)} = Q^2 \frac{2 \left( 40 \ell^4 + 80 \ell^3 + 30 \ell^2 - 10 \ell - 3 \right)}{3n^3 (2 \ell + 3)(2 \ell + 1)(2 \ell - 1) \ell^2 (\ell + 1)^2}. \] (7.53)

The second-rank tensor term is

\[ \langle \psi_{nl\ell} | V_{22} | \psi_{nl\ell} \rangle^{(2,k=2)} = Q^2 \frac{a_{22}^{(k=2)}}{b_{22}^{(k=2)}} \{ \ell (\ell + 1) - 3 \lambda^2 \}, \] (7.54)

in which

\[ a_{22}^{(k=2)} = 10 \left( 560 \ell^6 + 1680 \ell^5 + 840 \ell^4 - 1120 \ell^3 - 777 \ell^2 + 63 \ell + 45 \right), \]
\[ b_{22}^{(k=2)} = 2n^3 (2 \ell + 3)^3 (2 \ell + 1)^3 (2 \ell - 1)^3 \ell^3 (\ell + 1). \] (7.55)

The fourth-rank tensor term is

\[ \langle \psi_{nl\ell} | V_{22} | \psi_{nl\ell} \rangle^{(2,k=4)} = Q^2 \frac{a_{22}^{(k=4)}}{b_{22}^{(k=4)}} \{ 35 \lambda^4 - 5(6 \ell (\ell + 1) - 5) \lambda^2 + 3(\ell + 2)(\ell - 1) \ell (\ell + 1) \}, \] (7.56)

in which

\[ \begin{align*}
  a_{22}^{(k=4)} &= 560 \ell^8 + 2240 \ell^7 - 7000 \ell^6 - 28840 \ell^5 - 19537 \ell^4 + 11606 \ell^3 + 10497 \ell^2 - 486 \ell - 540, \\
  b_{22}^{(k=4)} &= 7n^3 (2 \ell + 5)(2 \ell + 3)^5 (2 \ell + 1)^3 (2 \ell - 1)^3 (2 \ell - 3) \ell^3 (\ell + 1)^5 (\ell - 1)(\ell + 2).
\end{align*} \] (7.57)

The second-order dipole-octupole cross term contributes effective matrix elements of ranks 2 and 4. The second-rank tensor term is

\[ \langle \psi_{nl\ell} | V_{13} | \psi_{nl\ell} \rangle^{(2,k=2)} = -\mu \cdot O \frac{a_{13}^{(k=2)}}{b_{13}^{(k=2)}} \{ \ell (\ell + 1) - 3 \lambda^2 \}, \] (7.58)

in which

\[ \begin{align*}
  a_{13}^{(k=2)} &= 4 \left( 560 \ell^8 + 2240 \ell^7 + 4760 \ell^6 + 6440 \ell^5 + 1799 \ell^4 - 4522 \ell^3 - 2700 \ell^2 + 261 \ell + 162 \right), \\
  b_{13}^{(k=2)} &= n^3 \sqrt{21} (2 \ell + 3)^4 (2 \ell + 1)^4 (2 \ell - 1)^4 \ell^3 (\ell + 1)^3 (\ell + 2)(\ell - 1).
\end{align*} \] (7.59)
The fourth-rank tensor term is

\[
\langle \psi_{m_1} | V_{13} | \psi_{m_2} \rangle^{(2, k=4)} = - (\mu \cdot O) \cdot \frac{d_{13}^{(k=4)} \cdot b_{13}^{(k=4)}}{c_{13}^{(k=4)}} \times \left\{ 35 \lambda^4 + 5(6\ell(\ell+1)-5) \lambda^3 + 3(\ell+2)(\ell-1) \ell (\ell+1) \right\}, \tag{7.60}
\]

in which

\[
\begin{align*}
d_{13}^{(k=4)} &= \frac{2}{\sqrt{7} \ n^3} \\
b_{13}^{(k=4)} &= 2240 \ell^{10} + 11200 \ell^9 + 11760 \ell^8 - 20160 \ell^7 - 48636 \ell^6 \\
&\quad - 28308 \ell^5 + 10921 \ell^4 + 23102 \ell^3 + 8235 \ell^2 - 1314 \ell - 540 \\
c_{13}^{(k=4)} &= (2\ell + 5)(2\ell + 3) \ell(2\ell + 1)^2 (2\ell - 1)^4 (2\ell - 3) \ell^3 (\ell + 1)^3 (\ell - 1)^2 (\ell + 2)^2.
\end{align*}
\tag{7.61}
\]

Note that the equation for the second-order electric dipole matrix element derived using this method, Eq. (7.52), is exactly equal to the matrix element derived by Watson, given in Eq. (7.8).

A full account of higher-order polarization interactions has been given in a long series of papers by Lundeen and co-workers [19-27].

### 7.1.3 General Method for Separation of Fields

Using the extended long-range model, it is in principle possible to separately and precisely determine the value of each of the multipole moments and polarizabilities for any molecule, given sufficient sensitivity of the data in question. The most straightforward method is to fit the energy levels directly to a tensor expansion of an effective Hamiltonian with diagonal matrix elements.

\[\text{Section 7.1.3 was inspired by the work of Dabrowski et al [6-10].}\]
\[
E_{n\ell\lambda} = \frac{C^{(0)}}{n^3} + \frac{C^{(2)}}{n^2} \left\{ \ell(\ell + 1) - 3\lambda^2 \right\} \\
+ \frac{C^{(4)}}{n^2} \left\{ 35\lambda^4 - 5(6\ell(\ell + 1) - 5)\lambda^2 + 3(\ell + 2)(\ell - 1)\ell(\ell + 1) \right\} \\
+ \frac{C^{(6)}}{n^2} \left\{ 5\ell^2(63\lambda^4 + 84\lambda^2 + 4) + 15\ell(21\lambda^4 + 35\lambda^2 + 4) - 21\lambda^2(11\lambda^4 + 35\lambda^2 + 14)

- 5\ell^2(21\lambda^2 + 5) - 15\ell^3(14\lambda^2 + 5) + 5\ell^6 + 15\ell^5 \right\} \\
+ \eta \cdot B \left[ N(N + 1) + \ell(\ell + 1) - 2\lambda^2 \right]
\] (7.62)

and off-diagonal elements

\[
\langle N\ell\lambda | \hat{H}_n | N\ell\lambda \pm 1 \rangle = -\eta \cdot B \sqrt{N(N + 1) - \lambda(\lambda \pm 1)} \sqrt{\ell(\ell + 1) - \lambda(\lambda \pm 1)} \cdot F .
\] (7.63)

Assuming that the rotational constant of the ion core \( B \) is known with sufficient accuracy, this Hamiltonian has five adjustable parameters: the four tensor coefficients \( C^{(0)}, C^{(2)}, C^{(4)}, \) and \( C^{(6)} \) which arise from the electrostatic interactions, and one parameter \( \eta \) which arises from rotation-electronic interactions. After fitting the data to this expansion, each tensor coefficient resulting from the fit is equated with a sum of all nonzero matrix elements of a common tensor rank. This gives a system of equations which can be solved to determine the multipole moments and polarizabilities.

The most important consideration in this respect is to ensure that the multipole moments and polarizabilities can be separated using the data at hand. This can be difficult because the adiabatic dipole and quadrupole polarization operators have the same angular dependence as the electric dipole and quadrupole operators, and therefore in general their effects cannot be separated from one another from a set of data in which only one value of \( \ell \) represented. The radial parts of the matrix elements are different, however, and this gives their matrix elements a dramatically different dependence on \( \ell \) and a mildly different dependence on \( n \). The separation of multipole moments and polarizabilities can therefore either be accomplished
through (i) a simultaneous fit of Rydberg states with different values of the
orbital angular momentum $\ell$ (for example, a simultaneous fit of all
components of 10f and 10g) or (ii) by simultaneously fitting states with
identical $\ell$ but spanning a wide range of $n$ (for example, fitting all states
with $\ell=3$ and $5 < n < 15$).

Assuming that the data in question span at least two values of $\ell$ or a
wide range of $n$, there should be at least as many equations as unknown
variables in the aforementioned set of simultaneous equations. In general, at
a laser resolution of between $0.03$ cm$^{-1}$ (typical for high-resolution
nanosecond pulsed lasers) and $0.001$ cm$^{-1}$ (typical for pulse-amplified
continuous-wave lasers), the tensor coefficients should be sensitive to the
isotropic polarizability, anisotropic polarizability, the electric dipole moment,
the electric quadrupole moment, and the electric octupole moment for f
states and the isotropic polarizability, anisotropic polarizability, the electric
dipole moment and the electric quadrupole moment for g states. This would
provide approximately six measurable tensor coefficients and two measurable
orbit-rotation drag parameters, a total of approximately eight equations in
exactly six unknowns, and the set of equations should therefore be soluble.

It is also worth emphasizing that the orbit-rotation drag parameter of
Eqs. (7.28) and (7.29),

$$\eta = \left[1 - \frac{\mu^2}{2\ell^2(\ell+1)^2}\right]$$  \hspace{1cm} (7.64)

in principle allows convenient separation of the electric dipole and
quadrupole moments, which contribute to the second-rank tensor coefficients
with identical $\ell$ and $n$-dependence.
7.1.4 Separation of Fields in CaF

The \( n_f \) and \( n_g \) Rydberg states identified in Chapter 4 were fit to an effective Hamiltonian using the matrix elements given in Eqs. (7.62) and (7.63). Three fit iterations were required in the case of the \( n_f \) states and two were required in the case of the \( n_g \) states. The effective tensor coefficients \( C^{(i)} \) and orbit-rotation drag coefficients \( \eta \) for the 13f and 13g complexes are summarized in Table 7-3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>13f</th>
<th>13g</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C^{(0)} )</td>
<td>-3708.63 ±25.59</td>
<td>-1412.99 ±26.79</td>
</tr>
<tr>
<td>( C^{(2)} )</td>
<td>1182.81 ±5.34</td>
<td>355.53 ±3.58</td>
</tr>
<tr>
<td>( C^{(4)} )</td>
<td>10.65 ±0.23</td>
<td>-</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.9752 ±0.0009</td>
<td>0.9989 ±0.0006</td>
</tr>
</tbody>
</table>

Table 7-3. Effective tensor coefficients derived from fits of the 13f and 13g complexes.

The first long-range interaction which can be separated using the effective tensor coefficients determined from the fit is the isotropic polarizability. Whereas the scalar contributions of the permanent electric multipole fields for the \( n_f \) states, assuming point-charge behavior, are on the order of 0.1 cm\(^{-1}\), the same contributions to the electronic structure of the \( n_g \) states are approximately one order of magnitude smaller and will be unobservable at the resolution of the experiments described in this work. Thus, for the \( n_g \) states, the entire scalar contribution effectively arises from the isotropic dipole polarizability. Equating the scalar tensor coefficient for
the $ng$ states with the expression for the isotropic dipole polarization matrix
element, Eq. (7.16), gives an isotropic polarizability of $\alpha = 14.87 \pm 0.28$ au.

The next step in the analysis involves separating the electronic splittings due to the anisotropic multipole fields from the electronic splittings due to the anisotropic dipole polarizability. In principle this is accomplished using the second-rank tensor coefficients. For both the $nf$ states and $ng$ states, the electric dipole moment, electric quadrupole moment, and anisotropic dipole polarization terms give rise to the primary second-rank tensor contributions. Therefore, to the extent that the long-range model is valid, the second rank tensor coefficients may be equated with the matrix elements of the contributing long-range interactions to determine $\mu$, $Q$, and $\gamma$:

$$\frac{C^{(2)}_{\ell, n}}{n^3} = \left( \mu^2 - Q \right) \frac{2}{n^2 (2\ell + 3)(2\ell + 1)(2\ell - 1)\ell(\ell + 1)} - \gamma \frac{4\ell(\ell + 1) - 3n^2}{3n^5 (2\ell + 3)^3 (2\ell + 1)(2\ell - 1)^2 \ell(\ell + 1)}$$

or, explicitly for $\ell = 3$ and $\ell = 4$,

$$\begin{cases}
C^{(2)}_{\ell=3} = \left( \mu^2 - Q \right) + 0.0437\gamma \\
C^{(2)}_{\ell=4} = \left( \mu^2 - Q \right) + 0.0250\gamma
\end{cases} \quad (7.66)$$

Unfortunately, the anisotropic polarizability determined using Eqs. (7.66) and the tensor coefficients determined from the fitted data is unreasonably large (approximately 50 au) and implies, in combination with the isotropic polarizability determined above, that the polarizability of the CaF$^+$ core in a direction perpendicular to the internuclear axis [$a_\perp$; see Eqs. (18) and (19)], is negative, which is an unphysical result.
The reason for this apparent discrepancy is quite simply that the $mf$
states of CaF are not exactly nonpenetrating. Some additional level shifts
and splittings exist and are due to core-penetration effects, which are by
definition outside the scope of the long-range model. We arrive at this
conclusion for several reasons. First of all, an anisotropic polarizability of 50
au for CaF$^+$ is quite unexpected; calculations [28, 29] of the anisotropic
polarizabilities of the alkali fluorides and chlorides predict anisotropic
polarizabilities of 0 to ~10 au for first-, second-, and third-row fluorides and
chlorides (smaller for lighter fluorides and larger for heavier chlorides). The
behavior displayed by the alkali halides should be quite similar to that of
CaF$^+$ and especially so for KF, which is isoelectronic with CaF$^+$. According
to the calculations, the anisotropic polarizability of KF is approximately 1.5
atomic units [28] and its dipole moment is approximately 3.35 atomic units.
For comparison, the dipole moment of CaF$^+$ is calculated to be almost
exactly 3.35 atomic units using ab initio methods (see Table 7-4 below). It
is therefore reasonable to expect that the anisotropic polarizability should be
approximately 1.5 atomic units, and can be no larger than 5 atomic units.
An anisotropic polarizability of 5.0 atomic units would give level splittings
on the order of 0.1 cm$^{-1}$ for 13f, which would be small but detectable at our
resolution and precision. By contrast, the discrepancies here between the
observed and predicted behavior, as we will see below, are on the order of
1.0 cm$^{-1}$. The observed deviations therefore cannot be due to the anisotropic
polarizability, and as discussed above, higher-order polarization terms should
be entirely negligible.

It is also possible to rule out higher-order multipole moments as the
cause of the deviations. The electric multipole moments of CaF$^+$, which
have been calculated by S. Coy [30] using three separate methods, are listed
in Table 7-4. Shown in the table are the multipole moments calculated using (i) the point charge model, which assumes that the Ca$^{2+}$ and F$^-$ nuclei are point charges separated by the equilibrium internuclear distance of 3.54 a$_0$, (ii) a pseudopotential representation of the field of the core, similar to that used by Arif, Jungen, and Roche [31], and (iii) an all-electron *ab initio* method, which explicitly accounts for interactions between the Rydberg electron and all of the core electrons. The point charge multipole moments represent an upper bound on the magnitude of the actual CaF$^+$ multipole moments, since according to Eq. (8.5), any delocalization of charge (i.e. representation of the core electrons as a diffuse charge distribution, rather than point charges) will give rise to a reduction in the actual value of the multipole moments. The all-electron *ab initio* moments, on the other hand, are to be regarded more as a reasonable estimate. Taking the point charge moments as the maximum possible values, it is possible to calculate an upper bound for the matrix elements of each multipole operator. These are shown in Table 7-5.

As the Table shows, the matrix elements of the octupole and hexadecapole operators can be no larger than 0.25 cm$^{-1}$ for 13f. This is still at least four times smaller than the observed deviations, and the higher-order fields therefore cannot account for even a majority of the observed deviations in the nf states.

<table>
<thead>
<tr>
<th>Moment</th>
<th>Point Charge Model</th>
<th>One-Electron <em>ab initio</em></th>
<th>All-Electron <em>ab initio</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Monopole</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Dipole</td>
<td>-4.68</td>
<td>-3.47</td>
<td>-3.36</td>
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<tr>
<td>Quadrupole</td>
<td>-3.15</td>
<td>-0.15</td>
<td>-0.87</td>
</tr>
<tr>
<td>Octupole</td>
<td>-16.78</td>
<td>-1.18</td>
<td>-5.01</td>
</tr>
<tr>
<td>Hexadecapole</td>
<td>-29.76</td>
<td>12.89</td>
<td>-7.15</td>
</tr>
</tbody>
</table>

*Table 7-4:* Multipole moments calculated according to the point charge, one-electron *ab initio*, and all-electron *ab initio* models. Calculations performed by S. L. Coy [30].
<table>
<thead>
<tr>
<th>Order</th>
<th>Term</th>
<th>Rank</th>
<th>Magnitude, $\ell=3$</th>
<th>Magnitude, $\ell=4$</th>
<th>Magnitude, $\ell=5$</th>
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<tbody>
<tr>
<td>1</td>
<td>Quadrupole</td>
<td>2</td>
<td>-2.00</td>
<td>-0.908</td>
<td>-0.4890</td>
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<tr>
<td></td>
<td>Hexadecapole</td>
<td>4</td>
<td>-0.27</td>
<td>-0.036</td>
<td>-0.0076</td>
</tr>
<tr>
<td>2</td>
<td>Dipole</td>
<td>0</td>
<td>0.00</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>13.90</td>
<td>6.315</td>
<td>3.4001</td>
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<tr>
<td></td>
<td>Quadrupole</td>
<td>0</td>
<td>0.04</td>
<td>0.006</td>
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<td></td>
<td>Dipole-Octupole</td>
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<td></td>
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<td>4</td>
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<td>Octupole</td>
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<td>Polarizability</td>
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</tbody>
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Table 7-5: Magnitudes of matrix elements of multipole operators, assuming point-charge multipole moments, for the $n=13$ Rydberg states of CaF. The orders of the matrix elements are indicated in the Table, as well as their magnitudes for $\ell=3$, $\ell=4$, and $\ell=5$.

Finally, it may be argued that that the $nf$ states of CaF are slightly core-penetrating by estimating the fraction of the electron wavefunction that lies inside the core, using simple hydrogenic wavefunctions. Approximating the core boundary as a spherical surface with a radius of 5 $a_0$ (approximately the distance between the Ca$^{2+}$ nucleus and the outer edge of the F$^-$ ion), the fraction of a hydrogenic 13s orbital lying inside the core is approximately 9.7 \times 10^{-4}, or approximately 0.1%. Similarly, the fractions for 13p, 13d, 13f, and 13g are 9.9 \times 10^{-4}, 9.1 \times 10^{-4}, 8.5 \times 10^{-5}, and 1.9 \times 10^{-6}, respectively, and the corresponding percentages are approximately 0.1%, 0.1%, 0.01%, and
0.0001%. The penetration fractions for 13s, 13p, and 13d are therefore approximately equal, whereas the fraction for 13f is an order of magnitude lower, and the fraction for 13g is three orders of magnitude lower. On these grounds we would therefore expect the nf states to be very weakly penetrating, and the ng states to exhibit almost completely nonpenetrating behavior.

Since the nf states exhibit some symptoms of core penetration, it is not possible to apply the long-range models described in Chapters 7.1.1 and 7.1.2. On the other hand, the nh states, at our experimental resolution, will not provide accurate estimates of any of the higher-order electric multipole moments or the anisotropic polarizability simply because their matrix elements for \( \ell = 5 \) are too small. We are therefore unable to rigorously determine a value for the anisotropic dipole polarizability.

However, the ng states are still amenable to a fit using the long-range model, and we may still use them to determine an accurate value of \( (\mu^2 - Q) \). As noted above, it is reasonable to assume that \( \gamma \approx 1.5 \text{ au} \), which gives electronic splittings on the order of 0.02 \text{ cm}^{-1}, significantly below our sensitivity limit. We may therefore make the approximation

\[
C_{\ell=4}^{(2)} = (\mu^2 - Q) + 0.0250 \gamma \approx (\mu^2 - Q),
\]

which gives \( (\mu^2 - Q) = 11.23 \pm 0.11 \text{ au} \).

While it is not possible, on the basis of the data described here, to determine values for the higher-order multipole moments, such a determination should be possible using higher-resolution sources and/or in ultra-high resolution experiments such as those described by Merkt and co-workers [32-35].
The observed levels of several of the \( nf \), \( ng \), and \( nh \) complexes have been plotted against the long-range model using the fitted values of \( (\mu^2 - Q) \) and \( \alpha \) in Chapter 4. As is evident in the figures, the agreement for the \( ng \) and \( nh \) states is striking, whereas nearly all of the \( nf \) states deviate significantly from long-range behavior, especially at low \( N \).

### 7.2 Long-Range Interactions in CaF

Having identified the discrepancies between the observed behavior of the \( nf \) states and that predicted by the long-range model as core-penetration effects, these effects will now be analyzed in detail.

For CaF, there are two possible zero-order pictures in which core-penetration effects can be understood: the hydrogenic framework and the ligand field theory (LFT) framework. In the hydrogenic framework, hydrogenic orbitals are taken as a starting point and all long-range and penetration effects are understood in terms of deviation from hydrogenic behavior. In the ligand field framework, which is only valid for ionic molecules, metal ion orbitals (in this case \( \text{Ca}^+ \)) are assumed to be mixed by the electric field of an attached ligand (in this case \( \text{F}^- \)), which is often treated as a point charge.

Penetration effects in the hydrogenic picture for the NO molecule have been discussed extensively in a paper by Jungen [11]. In the hydrogenic picture, deviations from the long-range model arise from five sources: (i) increased effective nuclear charge \( Z_{\text{eff}}(r) > 1 \) experienced by the Rydberg electron inside the core, (ii) exchange interactions between the Rydberg and core electrons, (iii) nonorthogonality of the Rydberg and core
electron orbitals, (iv) $\ell$-mixing of the Rydberg orbitals at short range by the electric field of the core, and (v) electron correlation. The first effect, increased effective nuclear charge, is due to the incomplete screening of the nucleus by the core electrons when the electron enters the core region. It is always a stabilizing effect (i.e. contributes positively to the quantum defect). The second and third effects arise due to the nonzero overlap between the Rydberg electron and core electron orbitals. The exchange interaction is likewise always stabilizing. The nonorthogonality effect represents an attempt by the molecule to satisfy the Pauli exclusion principle, and gives rise to “Pauli repulsion”. Pauli repulsion is always a destabilizing effect.

The fourth effect, $\ell$-mixing of the Rydberg orbitals at short range, is simply the result of the Rydberg electron entering the nonspherical Hartree-Fock field of the ion core. It is distinct from $\ell$-mixing at long range in the sense that when $r$ is on the order of $R$, the multipole expansion of Eq. (8.4) is not valid and cannot be used to calculate the matrix elements of the electrostatic interactions at short range. Finally, the fifth effect, electron correlation, involves the concerted motion of two electrons which, in Rydberg molecules, implies electronic excitation of the core.

In CaF, the core (in its ground electronic state) consists of two closed-shell ions, Ca$^{2+}$ and F$^-$. Penetration into the fluoride ion, with its overall negative charge, is unlikely to occur and therefore the Rydberg electron should experience no increased effective nuclear charge due to the presence of the fluorine nucleus. However, exchange always occurs to some extent, and nonorthogonality of with the occupied F$^-$ 2p orbitals must be considered for $\sigma$ and $\pi$ Rydberg orbitals, regardless of $\ell$. The presence of the F$^-$ ion also gives rise to a strong inhomogeneous electric field which will significantly
mix Rydberg orbitals of any symmetry. Penetration into the positively-charged Ca\(^{2+}\) ion is significant, especially for states with \(\ell < 3\), and therefore increased effective nuclear charge and exchange must be considered in the hydrogenic picture. Since the s and p core orbitals of the Ca\(^{2+}\) ion are occupied, the possible nonorthogonality of s and p Rydberg orbitals must also be considered. Finally, effect (v), electron correlation, is a potential source of deviations from hydrogenic behavior in the sense that the Rydberg electron can excite the core and transfer charge from the F\(^{-}\) to Ca\(^{2+}\), leading to the Ca\(^{+}\)F\(^{0}\) configuration, which is unstable and will typically lead to dissociation of the molecule into neutral Ca and F fragments.

In the ligand field picture, on the other hand, many of these effects are already accounted for in zero-order. Since the starting point of the ligand field picture is the set of eigenstates of the potassium-like Ca\(^{+}\) ion, all effects associated with penetration into the Ca\(^{2+}\) closed shell core are already accounted for. Therefore, only the effects due to the presence of the F\(^{-}\) ion need be considered. The ligand field picture will thus be adopted as the zero-order framework, since this will considerably simplify our discussion of penetration effects.

The observed levels of the 13f and 15f complexes and their positions calculated using the parameters determined above are shown in Chapter 4. As the figures show, the centers of gravity of the f complexes (located approximately at the high-\(N\) asymptote of the \(\Delta\) component), match the calculations almost perfectly. The measured isotropic polarizability gives, for the f states of CaF, an isotropic contribution to the quantum defect of 0.023, which is in excellent agreement with the quantum defect of 0.025 for the f series of Ca\(^{+}\). In Ca\(^{+}\) the quantum defect of the f series is known to be caused almost entirely by the polarization interaction, and we can therefore
conclude that the polarization interaction with the Ca$^{2+}$ core is responsible for the isotropic shift observed here, and the F$^-$ ion contributes very little in this respect.

While the isotropic shift of the complex is accounted for in zero order, almost all components of the 13f and 15f complexes deviate significantly from their expected positions. The $\Sigma^+$, $\Pi^+$, $\Pi^-$, $\Phi^+$, and $\Phi^-$ components all lie higher in energy than the long-range model predicts, and the $\Delta^+$ and $\Delta^-$ components lie slightly lower in energy than the long-range model predicts. The 14f, 16f, and 17f complexes, shown in the supplementary material, obey the same trends. Thus, while the scalar contribution to the $\ell = 3$ quantum defects is almost entirely due to long-range interactions with the Ca$^{2+}$ core, the tensor contributions are due partly to the long-range fields and partly to short-range interaction with the F$^-$ ion. As noted above, the additional short-range interactions with F$^-$ can arise from exchange, nonorthogonality, $\ell$-mixing, and electron correlation. Since the 2p shell of the F$^-$ ion is closed, exchange should be negligible. Pauli repulsion, which is a destabilizing interaction, is only a source of concern for the $\Sigma$ and $\Pi$ components. As both of these components of the f complexes lie significantly higher in energy than predicted by the long-range model, it is likely that at least part of the discrepancy is accounted for by Pauli repulsion due to nonorthogonality of the Rydberg and F$^-$ orbitals.

The bulk of the deviations from long-range behavior, however, are most likely due to $\ell$-mixing at short range. The $\Delta$ and $\Phi$ components of the f complex, by symmetry, cannot suffer the effects of electron correlation or nonorthogonality, and the only source of deviation is therefore $\ell$-mixing, which can be a stabilizing or destabilizing interaction. Since this $\ell$-mixing
causes deviations from long-range behavior for $f\Delta$ and $f\Phi$ that are similar in magnitude to the deviations for $f\Sigma$ and $f\Pi$, it appears likely that the bulk of all of the penetration effects in the $f$ complexes are accounted for by $\ell$-mixing at short range.

### 7.3 Short-Range Interactions in CaF

The discussion presented in Chapter 7.2 allows one to proceed toward an understanding of what fractions of the (much larger) quantum defects of the core-penetrating ‘s’, ‘p’, and ‘d’ series of CaF are due to long-range interactions and what fractions are due to penetration effects.

Of all of the series of CaF with $\ell < 3$, the $nd$ states should exhibit the weakest penetration effects and should therefore be most amenable to the perturbation treatment employed in this investigation. Of the three, the $d\Delta$ series of CaF should be the most weakly penetrating, and by symmetry can only be affected by $\ell$-mixing at short range. The quantum defects of the $d\Sigma$, $d\Pi$, and $d\Delta$ series of CaF and their origins are summarized in Table 7-6. The quantum defect of the d series of Ca$^+$ is 0.62 [36], and the quantum defects of the $d\Sigma$, $d\Pi$, and $d\Delta$ series of CaF are -0.19, 1.02, and 0.86, respectively. The long-range contributions to the quantum defects (including only the contributions due to the electric dipole and quadrupole fields) are -0.22, -0.11, and 0.21, which means that the short-range contributions for $\Sigma$, $\Pi$, and $\Delta$ are -0.59, 0.51, and 0.03. Thus, the $d\Delta$ series of CaF is indeed a long-range state and exhibits only very weak core penetration. On the other hand the $\Sigma$ and $\Pi$ series, as expected, are much more strongly core-penetrating.
<table>
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<tr>
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<th>Ca$^+$</th>
<th>Long Range</th>
<th>Short Range</th>
</tr>
</thead>
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<td>0.62</td>
<td>-0.22</td>
<td>-0.59</td>
</tr>
<tr>
<td>dΠ</td>
<td>1.02</td>
<td>0.62</td>
<td>-0.11</td>
<td>0.51</td>
</tr>
<tr>
<td>dΔ</td>
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<td>0.62</td>
<td>0.21</td>
<td>0.03</td>
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</tbody>
</table>

**Table 7-6.** Contributions to the quantum defects for d ($\ell = 2$) states.

As shown in the figures in the appendix at the end of this chapter, while the agreement of the perturbation method is excellent for f and g states, the agreement is reasonable for d states and is rather poor for s and p states. However, the contributions to the quantum defects from the dipole field can be determined exactly, and for the sake of the following discussion it will be assumed that the dipole field is the only long-range interaction that contributes significantly to the quantum defects. The quantum defects of the sΣ, pΣ, and pΠ series of CaF and their origins are summarized in Table 7-7. As can be seen in the table, for the p states the long-range contributions from the dipole field are nearly as large as the short-range contributions, and at least in this case they are of opposite sign. For s states, it is not possible to analytically calculate the contribution from the dipole field when the dipole moment is greater than 0.64 atomic units [5], and thus for the s states we are not able to separate the long-range and short-range contributions.

<table>
<thead>
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<th>Long Range</th>
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</thead>
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<td>-1.23</td>
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</table>

**Table 7-7.** Contributions to the quantum defects for s ($\ell = 0$) and p ($\ell = 1$) states.
7.4 Ligand Field Theory

The ultimate goal of this work is to generate an explicit understanding of why the individual quantum defect matrix elements $\mu_{\ell'\ell}^{(\lambda)}$, $\frac{\partial \mu_{\ell'\ell}^{(\lambda)}}{\partial R}$, and $\frac{\partial \mu_{\ell'\ell}^{(\lambda)}}{\partial E}$ have the values that they do. It may be possible to use ligand field theory to accomplish this goal.

Ligand field theory [37-39] divides the molecular Hamiltonian into three parts:

$$H = H^{(Ca^+)} + H^{(LF)} - \frac{2e^2}{R}. \quad (7.68)$$

Here, $H^{(Ca^+)}$ is the Hamiltonian of the potassium-like Ca(II) ion, $H^{(LF)}$ is the ligand field Hamiltonian, and the third term represents the attraction between the Ca$^+$ and F$^-$ ions. The ligand field Hamiltonian

$$H^{(LF)} = \frac{e^2}{r_{12}} \quad (7.69)$$

describes how the Ca$^+$ atomic orbitals are split and mixed by the field of the fluoride ion. In a typical ligand field calculation, the matrix elements of (7.68) are calculated in a suitably large basis of Ca$^+$ eigenstates, and diagonalization of the Hamiltonian gives the eigenenergies of the molecule. The coordinate system employed is shown in Fig. 7-2.
To evaluate matrix elements of the ligand field operator (7.69), the law of cosines is used to express \( r_{12} \) in terms of \( R \), \( r \), and \( \theta \):

\[
r_{12}^2 = R^2 + r^2 - 2rR \cos \theta. \tag{7.70}
\]

Thus,

\[
\frac{1}{r_{12}} = \frac{1}{\sqrt{R^2 + r^2 - 2rR \cos \theta}}, \tag{7.71}
\]

which can be expanded using the multipole expansion:

\[
\frac{1}{r_{12}} = \sum_k \frac{r_<^k}{r_>^{k+1}} P_k(\cos \theta). \tag{7.72}
\]

Here, \( r_\geq \) and \( r_< \) represent, respectively, the greater and lesser of \( r \) and \( R \).

The matrix elements are thus

\[
\frac{1}{\sqrt{R^2 + r^2 - 2rR \cos \theta}} = \frac{1}{R} + \frac{r}{R^2} P_1(\cos \theta) + \frac{r^2}{R^3} P_2(\cos \theta) + \ldots
\]

\[
= \sum_k \frac{r_<^k}{R^{k+1}} P_k(\cos \theta)
\]

when \( r > R \), and

\[209\]
\[ \frac{1}{\sqrt{R^2 + r^2 - 2rR \cos \theta}} = \frac{1}{r} + \frac{R}{r^2} P_1(\cos \theta) + \frac{R^2}{r^3} P_2(\cos \theta) + \ldots \]  
\quad = \sum_k \frac{R^k}{r^{k+1}} P_k(\cos \theta) \tag{7.74} \]

when \( r < R \). The matrix elements are finally written as

\[ H^{(l,l')}_{n,n',\ell;\ell'} = \sum_k B_k(n\ell;n'\ell') c_k(\ell m;\ell'm') \tag{7.75} \]

where

\[ B_k(n\ell;n'\ell') = \int_0^R R_m(r) R_{m'}(r) \frac{r^k}{R_{k+1}} dr + \int_R^\infty R_m(r) R_{m'}(r) \frac{R^k}{r^{k+1}} dr \tag{7.76} \]

and

\[ c_k(\ell m;\ell'm') = \sqrt{\frac{2}{2k+1}} \int_0^\infty \Phi_{k0}(\theta) \Phi_{\ell m}(\theta) \Phi_{\ell'm'}(\theta) \sin \theta d\theta \tag{7.77} \]

It is useful to note that the above angular integral truncates the ligand field expansion; matrix elements are only nonzero when \( k \) takes on the values

\[ k = |\ell - \ell'|, |\ell - \ell'| + 2 \ldots (\ell + \ell') \tag{7.78} \]

It may be possible to derive the quantum defect matrix elements and their derivatives from ligand field theory since (i) Hartree-Fock wavefunctions for the \( \text{Ca}^+ \) orbitals are readily available, (ii) the quantum defects of the \( \text{Ca}^+ \) Rydberg states, as well as their dependences on energy, are known, (iii) ligand field theory explicitly states how the \( \text{Ca}^+ \) orbitals are mixed by the field of the \( \text{F}^- \) ligand, and (iv) the radial integrals in Eq. (7.76) dictate exactly how the ligand field mixing should depend on the internuclear distance. The main difficulty toward this end lies in the establishment of an explicit relationship between the mixing coefficients of the ligand field wave functions, which are properties of individual eigenstates, and the quantum defects, which are properties of entire Rydberg
series. If this difficulty can be surmounted, the resulting explicit interpretation of the quantum defects in terms of ligand field theory should allow the generation of deep insights into the short-range scattering processes in CaF and ultimately, an improved understanding of the electron-nuclear energy exchange processes that depend on them.
7.5 Appendix: Validity of Perturbation Method

Watson [5] shows that the Hamiltonian

$$\hat{H} = -\frac{1}{2} \nabla^2 - \frac{Z}{r} + \frac{\ell^2}{2r^2} - \frac{\mu \cos \theta}{r^2}$$

is exactly soluble in polar coordinates, and that the resulting quantum defects are

$$\delta_{\ell \ell'} = \ell + \frac{\mu}{2} - \sqrt{\frac{\ell(\ell+1)+\frac{2\mu^2}{\ell(\ell+1)^2+3\ell^2}}{\ell(\ell+1)(2\ell+1)(2\ell+3)}} + \frac{\mu}{4}\cdot$$

By contrast, the perturbative dipole treatment gives

$$\delta_{\ell \ell'} = -\frac{2\mu^2}{\ell(\ell+1)^2(2\ell+1)(2\ell+3)}.$$

The difference between the exact and perturbative quantum defects are compared in Figures 7-3 to 7-6 for $\ell = 1, 2, 3, \text{and } 4$, respectively.
Figure 7-3: Contribution of the dipole field to the quantum defects for $\ell = 1$, calculated as a function of $\mu^2$. Exact solution, solid lines; perturbative solution, dashed lines. Numbers in parentheses indicate the difference between the perturbative and exact solutions at $\mu^2 = 10$. 
Figure 7-4: Contribution of the dipole field to the quantum defects for $\ell = 2$. Numbers in parentheses indicate the difference between the perturbative and exact solutions at $\mu^2 = 12$. 
Figure 7-5: Contribution of the dipole field to the quantum defects for $\ell = 3$. Numbers in parentheses indicate the difference between the perturbative and exact solutions at $\mu^2 = 12$. 
Figure 7-6: Contribution of the dipole field to the quantum defects for $\ell = 4$. Numbers in parentheses indicate the difference between the perturbative and exact solutions at $\mu^2 = 12$. Stars indicate that the difference is less than 0.0001 quantum defect units.
7.6 Bibliography


Chapter 8

Conclusions

A global quantum defect model that accounts for nearly all possible dynamical processes in CaF has been constructed. The heart of the model consists of the 20 quantum defect matrix elements and their derivatives with respect to the internuclear distance and the collision energy of the Rydberg electron. Nearly all linear derivatives (20 with respect to internuclear distance, 16 with respect to energy) have been determined, as well as 35 quadratic derivatives, for a total of 91 parameters. The completion of this work pushes the CaF molecule to a level of characterization which parallels that of H₂ and NO.

The set of quantum defects presented here should allow theorists and experimentalists alike to ask (and answer) very deep questions about molecular structure and dynamics. Work along these lines has already been presented here. The equilibrium quantum defects have been used to examine the underlying classical dyanamics of the interaction between electronic and rotational motions in Rydberg states. Progress toward distillation of the physical content of the quantum defect parameters has likewise been presented.

Probably the most interesting prospect for future work in this area surrounds the subject of interpretation. If the quantum defect matrices and their dependence on $R$ can be derived from ligand field theory, for example,
it would allow one to understand the relative strengths of the various scattering processes and why these processes depend on internuclear distance and energy in the way that they do. Why, for example, are $d\sigma$ waves scattered into the $f\sigma$ channel and not the $p\sigma$ channel, and why do the elasticities of the $p\pi-p\pi$ and $d\pi-d\pi$ scattering processes depend so strongly on collision energy? Since these electronic scattering processes control all of the nonadiabatic electron-nuclear energy transfer processes, these are important questions.

Naturally, all of the questions that have been asked here can be also asked of larger molecules. But in the end, the author of this work hopes that he has demonstrated that the detailed study of the simplest molecular systems really does open the door to entirely new questions in the first place, and that many interesting questions about small molecules do still remain.