Spring 1977

CHARGE EXCHANGE OPTICAL PUMPING

SALLIE SLAWSON TOWNSEND

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Keywords
Physics, Atomic
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TOWNSEND, Sallie Slawson, 1944-
CHARGE EXCHANGE OPTICAL PUMPING.

University of New Hampshire,
Ph.D., 1977
Physics, atomic

Xerox University Microfilms, Ann Arbor, Michigan 48106

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CHARGE EXCHANGE OPTICAL PUMPING

by

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A THESIS
Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of

Doctor of Philosophy

Graduate School
Department of Physics

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ACKNOWLEDGMENTS

The author wishes to express her gratitude first and foremost to her thesis director Dr. John F. Dawson for his continuous guidance, encouragement, and support during the course of this research. She would also like to thank Dr. L. C. Balling for suggesting the investigation and Dr. Robert H. Lambert for his many years of invaluable tutelage in the field of optical pumping.

Special thanks go to Dr. John E. Mulhern for his continuing encouragement and to Dr. Robert E. Houston, Jr. without whose untiring support and personal guidance this work would not have been possible.

The author is indebted to Bonnie Lloyd for her special effort in typing and to Jerry Pierce for drafting the table and the illustrations.

Finally the author would like to thank her family and friends for their limitless patience and moral support.

This work was partially supported by the National Science Foundation.
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ABSTRACT

CHARGE EXCHANGE OPTICAL PUMPING

by

SALLIE S. TOWNSEND

The theory of resonant charge exchange optical pumping of an alkali atom is discussed. Using the perturbed stationary state approximation, a form of the scattering matrix is derived which includes the effect of the identical nuclei. With the assumptions of no ionic polarization, no hyperfine coherence, and the validity of the secular approximation the time dependence of the atomic density matrix is derived. The effects of other atomic relaxation mechanisms are then included. Finally, the specific example of charge exchange collisions between atomic and ionic Rb$^{87}$ is discussed.
CHAPTER I

INTRODUCTION

The experimental technique of optical pumping was first proposed by Kastler in 1950. He suggested that atoms, whose level populations would normally follow the Boltzmann distribution law, could be oriented by means of circularly polarized resonance radiation. Since then there have been numerous experiments using optical pumping directly to study atomic properties, and indirectly, by means of spin exchange or charge exchange collisions, to study properties of species which cannot be pumped directly.

Optical pumping consists of selectively pumping a sublevel of the ground state by means of absorption and reemission of light in the presence of a constant magnetic field. For example, consider the level structure of a fictitious alkali atom which has zero nuclear spin. Choosing the z axis to be the direction of the magnetic field and subsequently the direction of propagation of the pumping light, one finds that the ground state and first excited state have the levels as depicted in figure 1. Now assume the selected level is the $m = -\frac{1}{2}$ state. Then if one sends in polarized D1 resonant radiation $\sigma^-$, only one level of the ground state can absorb the light namely the $m = +\frac{1}{2}$ state. Since the light is assumed to be D1
2

\[ \Delta m = V_z m = -\frac{1}{2} \]

**Ground State**

- \( S_{1/2} \)
  - \( m = 1/2 \)
  - \( m = -1/2 \)

**Excited States**

- \( P_{3/2} \)
  - \( m = 3/2 \)
  - \( m = 1/2 \)
  - \( m = -1/2 \)
  - \( m = -3/2 \)

- \( P_{1/2} \)
  - \( m = 1/2 \)
  - \( m = -1/2 \)

**Figure 1**

Energy levels of a fictitious alkali atom with no nuclear spin.
only, this is the only transition from the $\frac{S}{2}$ to the $\frac{P}{2}$ state such that the atom loses one unit of angular momentum. Once in the excited state, the populations can be partially rearranged by collision. The atom in the excited state can then reemit a photon of either polarization, thus returning to either of the ground state sublevels. This process is shown in figure 2. The overall result is a decrease in the population of the $m = \frac{1}{2}$ sublevel and increase in the $m = -\frac{1}{2}$ level, as desired. Eventually, one could conceivably achieve 100% orientation of the ground state if there were no relaxation mechanisms trying to equalize the ground state populations.

The phenomenon of optical pumping has been advantageously utilized in various experiments. By pumping with D1 light only Franzen and Emslie\textsuperscript{2} were able to study the relaxation of oriented atoms. The hyperfine frequency and the effects of buffer gas density on this frequency have been investigated for many species.\textsuperscript{3,4,5,6,7} The relaxation effect of collisions of oriented atoms with various types of wall coatings was studied by M. Bouchiat and others.\textsuperscript{8,9,10,11,12} In 1958 Dehmelt\textsuperscript{13} performed an experiment which greatly broadened the field of optical pumping. He experimentally investigated the free-electron magnetic moment by spin exchange optical pumping. This was achieved by first optically pumping the ground state of sodium. Unpolarized electrons then collided with the sodium, simultaneously disorienting the sodium and orienting the free
a) The atoms are in Boltzmann equilibrium

b) The incident light is absorbed

c) The excited state is collisionally rearranged

d) The excited atoms deexcite by spontaneous emission

There is a net gain of two atoms in the \( m = -\frac{1}{2} \) ground state

**Figure 2**

The process of optical pumping
electrons. A resonant radio-frequency field was applied which again disoriented the free electrons so they could further disorient the sodium. Maximum disorientation of sodium and therefore maximum absorption of light from the incoming beam occurred when the rf field was tuned to the resonant frequency of the electrons, thereby yielding the free electron gyromagnetic ratio. Similar experiments have since been performed utilizing spin exchange collisions with other species. The theory for spin exchange collisions has been given by Balling, Hanson and Pipkin (referred to as BHP) and Grossetête. In 1959 Franzen described an experiment in which he could measure the spin relaxation of oriented Rb. This was accomplished by pumping the Rb, then turning off the pumping light to let the system evolve. The light was then turned back on at specified times so that the relaxation could be monitored. This method is referred to as "relaxation in the dark". Since then Bouchiat and Grossetête have suggested a slightly different experiment in which a very weak monitoring light was left on at all times. Only a few of the numerous experimental and theoretical developments in optical pumping have been mentioned here. For a more complete listing, the reader is referred to the bibliographies of any of the extensive optical pumping reviews such as Balling, Happer, Bernheim, or Cohen-Tannoudji and Kastler.

Recently another exchange process has become an
important method of orienting the spins of atomic systems. Charge exchange collisions can be used to investigate the properties of ions and nuclei especially those of the alkali atoms since their ions possess a $^1S_0$ electronic configuration. Although the phenomenon of charge exchange collisions has been known for a long time, \cite{29,30,31} recently there has been a great deal of interest in both non-resonant \cite{32,33,34,35,36,37,38,39} and resonant \cite{40,41,42,43,44,45} charge exchange collisions.

Resonant charge exchange can occur when an ion and its parent atom collide. Assume that in the center of mass system one has an atom coming in from the left and an ion from the right as depicted in figure 3. An ion is detected at the detector. Since the ions are identical, there is no way of distinguishing between them. The ion flux at the detector is then due to both the direct and exchange collisions. The calculation of the scattering amplitude for the process must therefore include the effects of the symmetry of the ions yet recognize that the ion and atom are distinct entities, not identical particles. The total amplitude for this process should be of the form

$$f(\theta) = f_{\text{direct}}(\theta) \pm f_{\text{exchange}}(\pi - \theta)$$

The apparatus used in charge exchange collisions is similar to that used in spin exchange collisions. For example, Mitchell and Fortson \cite{42,43} use the apparatus as seen in figure 4. Resonant light is produced in the lamp, then is passed through a filter and a circular
Figure 3

Charge Exchange Collisions
FIGURE 4

TYPICAL OPTICAL PUMPING APPARATUS
polarizer. The filter allows only the D1 light to pass to the resonance bulb in which there is alkali gas and He buffer gas at approximately 30 torr pressure. As the D1 light passes through the cell, the alkali atoms become oriented and the bulb becomes transparent. Alkali ions with a density of about $10^{10}$ ions/cc are produced in the sidearm. When these collide with the atoms, the atoms become disoriented. A constant magnetic field of 5-10 Gauss is produced by Helmholtz coils, while an r-f coil is set up to produce an r-f field orthogonal to the constant field. The constant field separates the magnetic substates of the atom and ion and the r-f field keeps the ions unpolarized.

Specifically the problem analyzed here is that of relaxation of the alkali atom density matrix due to charge exchange collisions. In chapter II a specific form of the interaction potential between the atom and the ion is not chosen. However, it is assumed that the identity of the two ions has an effect on the scattering cross section. The interaction potential $V(\mathbf{R})$ between the atom and the ion, assumed fixed at a position $\mathbf{R}$ for the validity of the adiabatic approximation, is very different depending on whether the ions and therefore the nuclei form a symmetrical or antisymmetrical state during the collision. Ion and nucleus can be used interchangeably here as far as angular momentum is concerned since the ion has a closed outer shell of electrons which do not interact. The analysis of the situation is complicated by the fact that
there is non-zero nuclear spin, and that the charge exchange
operator cannot be easily expressed in terms of spin
operators as was done by Grossetête\textsuperscript{20} in her analysis of
electron spin exchange collisions where she found
\[ \rho_{\sigma \tau} = \frac{\hbar}{2} (1 + \vec{s} \cdot \vec{\tau}) \] (1.1)
However, the result of a more general analysis in Chapter
III is an expression for the relaxation of the atomic
density matrix under the assumptions of the secular approx­
imation and no hyperfine coherence which is far more general
than the ones she derives. The effect of the non-zero
nuclear spin is that there are many more energy levels
in the ground state and excited state of the atom. For a
specific example, the energy levels of Rb\textsuperscript{87} ( I = 3/2 )
have been depicted in figure 5. Since the magnetic field
will be assumed to be weak, the hyperfine interaction, \( A \vec{F} \cdot \vec{J} \)
predominates. The atomic Hamiltonian is
\[ H = A \vec{F} \cdot \vec{J} - \mu_0 (g_e \vec{F} + g_f \vec{J}) \cdot \vec{H} \] (1.2)
Since \(|g_e|\) is much less than \(|g_f|\), the nuclear term
may be ignored. When the magnetic field is weak, the
Zeeman term can be evaluated by first order perturbation
theory to be
\[ -\mu_0 g_f \vec{F} \cdot \vec{H} \] (1.3)
where the Wigner-Eckart theorem, equation (A.5) in
Appendix A, yields
EXCITED STATES

GROUND STATE

FIGURE 5
ENERGY LEVELS OF Rb$^{87}$ (I = 3/2)
\[ g_F = g_\sigma \cdot \frac{\mathcal{F}(F+1) + s(I+1) - I(I+1)}{2F(F+1)} \]  
\hspace{1cm} (1.4)

For the case of Rb\textsuperscript{87} with \( s = \frac{1}{2} \) and \( I = \frac{3}{2} \), one finds \( g_F \) to be

\[ g_1 = -\frac{1}{2} \quad \text{and} \quad g_2 = \frac{1}{2} \]  
\hspace{1cm} (1.5)

The atomic Hamiltonian is then

\[ H = A \vec{F} \cdot \vec{S} - \mu_0 g_F \vec{F} \cdot \vec{H}_0 \]  
\hspace{1cm} (1.6)

with energy levels

\[ E_{F,M} = A \left[ \frac{\mathcal{F}(F+1) - I(I+1) - S(S+1)}{2} \right] - \mu_0 g_F H_0 M_F \]  
\hspace{1cm} (1.7)

After the effect of just charge exchange collisions is found, the contribution of other atomic interactions, such as wall and buffer gas collisions and the interaction with the pumping light are included in Chapter IV. The time dependence of the density matrix is then again found with these effects included. Finally, the specific example of Rb\textsuperscript{87} is discussed in Chapter V.
CHAPTER II

CHARGE EXCHANGE COLLISIONS

When considering a rearrangement collision, such as \( A + A^+ \rightarrow A^+ + A \), one must recognize that the problem is primarily a three body problem. Therefore, it is extremely difficult to solve. One standard approximation, valid for slow collisions between atoms and ions, is the perturbed stationary state (P.S.S.) method (also referred to as the adiabatic approximation). It is similar to the Born-Oppenheimer method for dealing with bound states of diatomic molecules. In this approximation it is assumed that the ionic kinetic energies are so small compared with the electronic energy that the problem is first solved with the ionic kinetic energy ignored completely, thereby making the ionic separation \( R \) a parameter not a dynamical variable. Then, if desired, the ionic kinetic energy can be treated as a perturbation. The approximation is a fairly good one in this case as electronic energies are typically on the order of a few electron volts and the collisions are occurring at room temperature.

In order to take advantage of the P.S.S. method, one must first transform to coordinates so that the ionic kinetic energy term can be dropped from the Schrödinger equation. Then assume a form for the wave function and apply the boundary conditions. Finally, form the density
matrix and sum over all unwanted coordinates, leaving an atomic spin space density matrix parameterized in terms of scattering phase shifts.

The Hamiltonian for the problem can be symbolically written in terms of the coordinates for the three particles:

\[ H = \frac{p_A^2}{2M_A} + \frac{p_B^2}{2M_B} + \frac{p_e^2}{2m_e} + V_A(\vec{r}_A) + V_B(\vec{r}_B) + \]
\[ + U(\vec{r}_B - \vec{r}_A) \quad (2.1) \]

where all the coordinates for the problem are defined in figure 6. In order to cast the Schrödinger equation into the correct form, two coordinate transformations must be made. First, one must transform to the center of mass of the ions and their vector separation:

\[ \vec{R}_{AB} = \frac{M_A \vec{r}_A + M_B \vec{r}_B}{M_{AB}} \quad \quad \vec{P}_A = \frac{M_A}{M_{AB}} \vec{P}_{AB} - \vec{P} \quad (2.2a) \]

\[ \vec{R} = \vec{r}_B - \vec{r}_A \quad \quad \vec{P}_B = \frac{M_B}{M_{AB}} \vec{P}_{AB} + \vec{P} \]

Then treat the center of mass of the ions as if it were one particle and combine it with the electron in the same fashion as the previous transformation:

\[ \vec{R}_{cm} = \frac{M_{AB} \vec{r}_{AB} + m_e \vec{r}_e}{M_{tot}} \quad \quad \vec{P}_{AB} = \frac{M_{AB}}{M_{tot}} \vec{P}_{cm} - \vec{P} \quad (2.2b) \]

\[ \vec{r} = \vec{r}_e - \vec{r}_{AB} \quad \quad \vec{p}_e = \frac{m_e}{M_{tot}} \vec{p}_{cm} + \vec{P} \]

Under these two transformations the Hamiltonian becomes

\[ H = \frac{p_{cm}^2}{2M_{tot}} + \frac{p^2}{2M} + \frac{p_e^2}{2\mu} + V_A(\vec{r}_A) + V_B(\vec{r}_B) + \]
\[ + U(\vec{R}) \quad (2.3) \]
Figure 6

COORDINATES
where
\begin{align}
M_{\text{rot}} &= M_A + M_B + m_e \\
M_{\text{AB}} &= M_A + M_B \\
\frac{1}{\mu} &= \frac{1}{M_{\text{AB}}} + \frac{1}{m_e} \\
\frac{1}{M} &= \frac{1}{M_A} + \frac{1}{M_B} 
\end{align}
(2.4)

and
\begin{align}
\vec{r}_a &= \vec{r}_e - \vec{r}_A = \vec{r} A + \frac{M_B}{M_{\text{AB}}} \vec{r} \\
\vec{r}_b &= \vec{r}_e - \vec{r}_B = \vec{r} - \frac{M_A}{M_{\text{AB}}} \vec{r}
\end{align}
(2.5)

In the coordinate representation, the Schrödinger equation is then (setting \( \hbar = 1 \)):
\[
\left\{ -\frac{\nabla_{\vec{r}}^2}{2 M_{\text{rot}}} - \frac{\nabla_{\vec{r}}^2}{2 M} - \frac{\nabla_{\vec{r}}^2}{2 \mu} + V_A (\vec{r}, \vec{r}) + V_B (\vec{r}, \vec{r}) + U (\vec{r}) \right\} \Psi (\vec{r}, \vec{r}, \vec{r}_{\text{cm}}) = E_{\text{tot}} \Psi (\vec{r}, \vec{r}, \vec{r}_{\text{cm}})
\]
(2.6)

Where \( E_{\text{tot}} \) is the total energy of the atom-ion system.

Note that the center of mass coordinate does not appear in the Hamiltonian and is therefore an ignorable coordinate. Total momentum is thus conserved during the scattering.

Remove the center of mass dependence by assuming that the wave function has the following form:
\[
\Psi (\vec{r}, \vec{r}, \vec{r}_{\text{cm}}) = e^{i \vec{r}_{\text{cm}} \cdot \vec{r}_{\text{cm}}} \Psi_E (\vec{r}, \vec{r})
\]
\[
\Psi_E (\vec{r}, \vec{r}) \text{ then obeys}
\]
\[
\left\{ -\frac{\nabla_{\vec{r}}^2}{2 M} - \frac{\nabla_{\vec{r}}^2}{2 \mu} + V_A (\vec{r}, \vec{r}) + V_B (\vec{r}, \vec{r}) + U (\vec{r}) \right\} \Psi_E (\vec{r}, \vec{r}) = E \Psi_E (\vec{r}, \vec{r})
\]
(2.7)
where \( E = E_{\text{tot}} - K_e^2 / 2 M_{\text{tot}} \) is the available energy in the center of mass system.

In general, equation (2.7) cannot be solved exactly. It is at this point that one employs the P.S.S. method. The first term in (2.7) is the relative kinetic energy of the two ions and may be assumed small; it is therefore ignored. This then allows one to write the equation

\[
\left\{ \frac{\partial^2}{\partial \mu^2} + \epsilon(R) - V_\beta(\vec{R}_A) - V_\beta(\vec{R}_B) \right\} \chi(\vec{R}, R) = 0 \tag{2.8}
\]

where \( \epsilon(R) \) is the energy of the electron for fixed ionic separation \( \vec{R} \), and \( \chi(\vec{R}, R) \) the associated eigenfunction. Note that this is the same as Mott and Massey's equation (XX.V.31). At this point ignore the complication of the identity of the ions. It will be included later.

Assume that before and after collision the atom is in its ground state. Then, for a given energy \( E \) there are two permissible asymptotic states; either the electron is associated with ion A or with ion B. The admissible solutions of (2.8) must therefore asymptotically approach either of these states or a linear combination of them:

\[
f_e(\vec{R}, R) = F_1(\vec{R}) \chi_1(\vec{R}, R) + F_2(\vec{R}) \chi_2(\vec{R}, R) \tag{2.9}
\]

where the \( F's \) are expansion coefficients and depends on the parameter \( \vec{R} \). Now that the general form of the solution is known, the effect of the identity of the ions can be taken into account. At this point spin must also be taken
into account. The interaction potential \( U(r) \) between the ions depends strongly on whether the two ions from a symmetric (total nuclear spin odd) or antisymmetric (even) state. As a result there are two molecular wave functions; one is symmetric under spatial exchange of the two nuclei (\( \chi_g \); the gerade state) and the other is antisymmetric (\( \chi_u \); ungerade). Since the center of mass wave function is clearly symmetric, and the spin and molecular wave functions possess symmetry properties, the expansion coefficients must also be symmetrized so that the total wave function is antisymmetric. To accomplish this, one must know more about the \( F \)'s. To determine an equation for \( F(r) \), use the assumed form of solution (2.9) in equation (2.7), as in section XV.2.21 of Mott and Massey. The resulting equation is

\[
\chi_g \left[ \nabla^2_R + \frac{\hbar^2}{2M(U(R) + \Delta \epsilon_g(R))} \right] F_g + 2 \nabla_R \cdot F_g \cdot \nabla_R \chi_g + \\
+ F_g \nabla^2_R \chi_g + \chi_u \left[ \nabla^2_R + \frac{\hbar^2}{2M(U(R) + \Delta \epsilon_u(R))} \right] + \\
+ 2 \nabla_R \cdot F_u \cdot \nabla_R \chi_u + F_u \nabla^2_R \chi_u = 0
\]

(2.10)

where

\[
E = \frac{\hbar^2}{2M} + \epsilon(\infty) ; \quad \Delta \epsilon_g(R) = \epsilon_g(R) - \epsilon(\infty)
\]

and

\[
\left\{ \nabla^2_R /2\mu - V_A (R) - V_B (R) + \epsilon_{gu}(R) \right\} \chi_{g, u} (R) = 0
\]

Since \( \chi_g \) and \( \chi_u \) possess opposite parity, any integral involving one of each is zero. Therefore, multiply equation (2.10) first by \( \chi_g \) and integrate over \( R \), then
do the same thing with $\mathcal{K}_\nu$. Using $\int d^2 \mathcal{K}_{j,\nu} \mathcal{K}_{\tilde{j},\nu} = 1$, one finds

$$\left\{ \nabla^2 - \frac{\alpha^2}{\ell^2} - 2 M \left( U(R) + A \epsilon_{g,\nu}(R) \right) \right\} F_{g,\nu}(R) = 0 \quad (2.11)$$

Equation (2.11) is a Schrödinger-like equation with "potential" $U(R) + A \epsilon_{g,\nu}(R)$ which vanishes for large $R$. Therefore $F_{g,\nu}(R)$ can be written asymptotically as

$$F_{g,\nu}(R) \to C \left\{ e^{i \ell \cdot \vec{R}} + \frac{e^{i \ell R}}{R} F_{g,\nu}(\ell, \theta) \right\} \quad (2.12)$$

where $C$ is the normalization constant and depends upon whether one uses continuous or box normalization.

Note that $F(R)$ contains the scattering angle information.

The symmetrized and normalized $F$ is

$$F_{g,\nu}(R) \to \frac{C}{\sqrt{2}} \left\{ e^{i \ell \cdot \vec{R}} - e^{i \ell \cdot \vec{R}} + \frac{e^{i \ell R}}{R} F_{g,\nu}(\ell, \theta) \right\} \quad (2.13a)$$

with

$$F_{g,\nu}(\ell, \theta) = F_{g,\nu}(\ell, \theta) \pm F_{g,\nu}(\ell, \pi - \theta) \quad (2.13b)$$

Denote by $\phi(R)$ the atomic wave function. Then

$$\mathcal{K}_d(\xi, R) \to \frac{1}{\sqrt{2}} \left[ \phi_A(\xi_+^+) + \phi_B(\xi_-^-) \right] \quad (2.14)$$

$$\mathcal{K}_{\nu}(\xi, R) \to \frac{1}{\sqrt{2}} \left[ \phi_A(\xi_+^+) - \phi_B(\xi_-^-) \right]$$
All ingredients for construction of the full wave function are now ready. The spatially symmetrized functions are

\[ \psi_e(\tilde{\pi}, \tilde{R}) = \Gamma_g(\tilde{R}) \chi_g(\tilde{\pi}, \tilde{R}) + \Gamma_u(\tilde{R}) \chi_u(\tilde{\pi}, \tilde{R}) \]  
\[ \psi_0(\tilde{\pi}, \tilde{R}) = \Gamma_g(\tilde{R}) \chi_g(\tilde{\pi}, \tilde{R}) + \Gamma_u(\tilde{R}) \chi_u(\tilde{\pi}, \tilde{R}) \]  

In the center of mass system the full wave function is

\[ \Psi^E(\tilde{\pi}, \tilde{R}; I, I_z, S) = \{ \psi_e(\tilde{\pi}, \tilde{R}) P_A + \psi_0(\tilde{\pi}, \tilde{R}) P_s \} |\chi_0\rangle \]  

where the \( P's \) are projection operators onto symmetric (\( P_s \)) and antisymmetric (\( P_A \)) spin states and where \( |\chi_0\rangle \) represents the initial spin state

\[ |\chi_0\rangle = \sum_{M_z} C(I, I_z, S; M_z) |SM_z; I, M_I, I_z, M_{I_z}\rangle \]

For large \( R \) (2.15) becomes

\[ \Psi^E(\tilde{\pi}, \tilde{R}; I, I_z, S) \underset{R \to \infty}{\longrightarrow} \frac{\psi_e(\tilde{\pi}, \tilde{R})}{R} \left[ I_z \Gamma_g(\tilde{R}) (P_0 + P_3) + \frac{e}{R} \left[ \left( \frac{e^0}{2} \right) P_A + \left( \frac{e^0 - e^u}{2} \right) P_s \right] \right] 
\]

\[ + \psi_0(\tilde{\pi}, \tilde{R}) \left[ -i \frac{\Gamma_u}{R} (P_0 - P_3) + \frac{e}{R} \left[ \left( \frac{e^0 - e^u}{2} \right) P_A + \left( \frac{e^0 - e^u}{2} \right) P_s \right] \right] \]  

Inspection of (2.17) will suggest that there is a better set of projection operators with which one can express the wave function. One of them is the identity operator

\[ I = P_s + P_A \]

and the other is the exchange operator

\[ P_{e x} = P_3 - P_A \]

The physical basis for its name will be clear from inspection of (2.19b). It has the effect of interchanging the nuclear spins.
\[ P_{\text{ex}} |I, m_I, m_e m_e\rangle = (P_s - P_a) |I, m_I, m_e m_e\rangle = (P_s - P_a) \sum_{I M} |I M\rangle \langle I M | I, m_I, m_e m_e\rangle \]

\[ = (P_s + P_a) \sum_{I M} |I M\rangle \langle I M | I, m_I, m_I m_I, m_e\rangle = |I_m m_I I, m_I m_e\rangle \]

In terms of these operators the wave function becomes

\[ \Psi_\epsilon^{(e, r)} (\bar{r}, \bar{R}; I, I_e s) \rightarrow \frac{C}{R^2} \left\{ \phi_A (\bar{r}_a) \left[ e^{i\frac{\bar{r} \cdot \bar{r}}{2}} + \frac{1}{R} \right] M (\bar{r}, \bar{R}) \right\} - \phi_B (\bar{r}_b) \left[ e^{-i\frac{\bar{r} \cdot \bar{r}}{2}} + \frac{1}{R} \right] M (-\bar{r}, -\bar{R}) P_{\text{ex}} \right\} |\psi_0\rangle \]

where

\[ M (\bar{r}, \bar{R}) = \frac{1}{2} \left( \left( f_{g} (\theta) + f_{a} (\theta) \right) P_A + \left( f_{g} (\theta) + f_{a} (\theta) \right) P_s \right) \]

\[ = \frac{1}{2} \left( \left( f_{g} (\theta) + f_{a} (\theta) \right) I - \left( f_{g} (\pi - \theta) - f_{a} (\pi - \theta) \right) P_{\text{ex}} \right) \]

\[ = f_{g} (\theta) - f_{a} (\pi - \theta) P_{\text{ex}} \]

as was suggested on page 6.

Now that the wave function is known, one can calculate the quantity of interest, namely \((d\rho/dt)\) spin space due to charge exchange collisions. Following the method of the \(E_1\) take the outer product of the wave function and trace over all unwanted coordinates leaving only spin dependence in the density matrix.

Since the two ions are identical, care must be taken when performing the trace; properly symmetrized basis states must be used. The correct states can most easily be found by:
looking at the asymptotic form of the wave function, ignoring the scattered term. In momentum space the initial and final wave functions can be written:

$$\left| \Psi_{z} \right> = \frac{1}{\sqrt{2}} \left\{ \left| \Psi_{z}^{+}; \phi_{A} \right> + \left| \overline{\Psi}_{z}^{+}; \phi_{B} \right> \right\} / \chi_{o} \right>$$

(2.20)

$$= \left| \phi_{z}^{+} \right>_{o} / \chi_{o} \right>$$

where \( \left| \phi_{z}^{+} \right>_{o} \) is an operator in spin space and

$$\left| \overline{\Psi}_{z}^{+} \right> = \frac{1}{\sqrt{2}} \left\{ \left| \Psi_{z}^{+}; \phi_{A} \right> + \left| \Psi_{z}^{+}; \phi_{B} \right> \right\} / \chi_{o} \right>$$

(2.21)

where

$$\langle \overline{R} | \Psi_{z}^{+} \rangle = c_{\Psi_{z}^{+}}(\overline{R}) = C \left\{ c_{\Psi_{z}^{+}} \right\} = 2 \left\{ c \frac{\mathbf{r}}{\mathbf{r}} + \frac{\mathbf{r}}{\mathbf{r}} \right\}$$

(2.22)

Since there are no other atomic states of interest besides the ground state, there is no sum over atomic states and the spin space density matrix after collision is

$$\rho = \sum_{z} o_{\phi} \left| \phi_{z}^{+} \right> \left< \overline{\Psi}_{z}^{+} \right| \left< \overline{\Psi}_{z}^{+} \right| / \chi_{o} \right>$$

(2.23)

One can take advantage of the symmetry properties of the inner products and the orthogonality of the atomic wave functions in (2.23). By orthogonality

$$o_{\phi} \left< \phi_{z}^{+} \right| \left< \overline{\Psi}_{z}^{+} \right> = \left( \frac{1}{\sqrt{2}} \right)^{2} \left\{ \left< z^{+}; \phi_{A} \right> + \left< z^{+}; \phi_{B} \right> \right\} \times$$

$$\times \left\{ \left| \Psi_{z}^{+}; \phi_{A} \right> + \left| \Psi_{z}^{+}; \phi_{B} \right> \right\} / \chi_{o} \right>$$

(2.24)

$$= \frac{1}{2} \left\{ \left< z^{+}; \Psi_{z}^{+} \right> + \left< z^{+}; \Psi_{z}^{+} \right> \right\} / \chi_{o} \right>$$
The two terms in brackets are equal to each other since the inner product must be invariant with respect to reflection of the coordinate system. Therefore

$$\rho < \phi^0 | \psi' > = < \phi' | \psi'^0 > | \chi_o > \quad (2.25)$$

Similarly

$$< \phi^0 | \phi' > \rho = < \chi_o | < \psi^0 | \chi' > \quad (2.26)$$

The resulting density matrix after collision is thus

$$\rho = \sum_{\phi^0} < \phi^0 | \psi' > \rho_0 < \psi^0 | \chi' > \quad (2.27)$$

where

$$\rho_0 = | \chi_o \rangle \langle \chi_o | \quad (2.28)$$

The problem therefore has an effective wave function

$$\psi_f^0 (\vec{r}; I, I_s) = \frac{\psi_f^0 (\vec{r})}{\sum_{\phi^0}} | \chi_o > \quad (2.29)$$

which may be treated as if there were no identical particles involved in the collision process. The effect of the antisymmetry of the nuclei is entirely contained within the scattering matrix $M$, equation (2.19).

If one were to say that $| \nu'_f > | \chi_o > = S' | \nu_f > | \chi_o >$

where

$$< \phi' | S' | \phi' > = \delta_{\nu' \nu} +$$

$$+ 2 \pi i \left( \frac{2 \mu I^2}{\mu_0 \hbar} \right) \delta (\vec{r} - \vec{r'}) < \phi' | H | \phi' >$$
then equation (2.27) is just equation (18) of BHP\textsuperscript{14}. Following their analysis, one then finds that the change in the density matrix due to charge exchange collisions is

$$\frac{\partial \rho}{\partial t} = \frac{\mathcal{U}_c}{\mathcal{G}} \left[ \frac{2\pi i}{k} (M(\theta)\rho - \rho M^+(\theta)) + \int d\theta \, \tilde{M}(\theta) \rho M^+(\theta) \right] \quad (2.31)$$

where the normalization factor $C$ was chosen to be $1/\mathcal{G}$. By expressing $M$ in terms of the gerade and ungerade phase shifts

$$\int d\omega \, U(\omega) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) \left( 2i \eta_{l}^{g} - 1 \right) \frac{P_{l}}{P \, \cos(\theta)} \quad (2.32)$$

which is legitimate because of the form of equation (2.12), one can write equation (2.31) in terms of these phase shifts. To see this, introduce the symmetric and antisymmetric scattering amplitudes

$$\begin{align*}
\mathcal{A}(\theta) &= \frac{1}{2} \left[ \mathcal{A}^{g}(\theta) + \mathcal{A}^{s}(\theta) \right] ; \\
\mathcal{B}(\theta) &= \frac{1}{2} \left[ \mathcal{B}^{g}(\theta) + \mathcal{B}^{s}(\theta) \right] \quad (2.33)
\end{align*}$$

so that

$$M(\theta) = \mathcal{A}(\theta) \, \mathcal{P}_A + \mathcal{B}(\theta) \, \mathcal{P}_S \quad (2.34)$$

These two amplitudes can also be expanded in terms of phase shifts since, for example, in $\mathcal{A}(\theta)$, $\mathcal{B}^{g}(\theta)$ provides all the even terms and therefore all the even phase shifts and $\mathcal{B}^{s}(\theta)$, the odd ones. Denoting these phase shifts by $\zeta^{g}_k$ and $\zeta^{s}_k$, one finds
\[
\frac{d\rho}{dt} = \nu_{\text{ee}} \frac{\sigma_{\text{ee}}}{\Omega} \left[ i \kappa \{ P_x, \rho \} + P_x \rho P_x - \rho \right]
\]  
(2.35)

where

\[
\sigma_{\text{ee}} = \frac{1}{4} \int \mathcal{J}^R \left| f_{s}(\theta) - f_{A}(\theta) \right|^2
\]

\[
= \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \left( \delta_l^S - \delta_l^A \right)
\]

and

\[
\kappa = \frac{1}{\sigma_{\text{ee}}} \cdot \frac{2\pi^2}{k^2} \cdot \sum_{l=0}^{\infty} (2l+1) \sin 2(\delta_l^S - \delta_l^A)
\]

Equation (2.35) thus gives the desired change in the spin space density matrix for like atoms and ions undergoing charge exchange collisions.

The formula for the scattering matrix \( M(\theta) \) derived here correctly corresponds to the previously published cross sections. Since they are given for spinless particles, set \( P_2 = 0 \) and \( P_A = 1 \) in the analysis to find an effective wave function for comparison purposes. Once the correspondence is made, one can see that, aside from normalization, the unsymmetrized wave function implied by (2.17) is the same as Mott and Massey's equation (XV.103). The charge exchange cross section (2.36) is seen to be the same as their equation (XV.111) and equation (54) of Massey and Smith. In order to see that the results agree with Geltman, one must first make the following correspondence between his notation and the notation used here

\[
\phi_{\text{Geltman}}^{e_0} = \phi_{\text{HERE}}^{e_0} / 2
\]

(2.38)
This can be seen to be true from several sets of corresponding equations, using the fact that
\[ e^\pm i Z \mathbf{R} = 2 \sum_{l=0,2,4,6,\ldots} f_l(\mathbf{R}) P_l(\mathbf{R} \cdot \mathbf{L}). \]

Here
\[
\begin{align*}
2.13a &\quad 23.17 \\
2.32 &\quad 23.18 \\
2.17 &\quad 23.21, 23.23
\end{align*}
\]

Geltman

His statement concerning the cross section formula (23.20) which is in the same paragraph as equation (23.23) is also correct: let \( \Theta \) go to \(-\Theta\) in the integral. Then
\[ \int dR \, f^+(\Theta) f^-(\Theta) = - \int dR \, f^+(\Theta) f^-(\Theta) = 0. \]

The total cross section for the spin zero case is then
\[
\sigma_{\text{TOT}} = \sigma_{\text{DIRECT}} + \sigma_{\text{EXCHANGE}} = 2 \sigma_{\text{EXCHANGE}} \quad (2.30)
\]

To find the total cross section for the case with nuclear spin, one must evaluate
\[
\frac{d\sigma}{d\Omega} = \mathcal{T} \mathcal{R}_{\text{INITIAL}} M^+ M \quad (2.40)
\]

for the case at hand. If one assumes that the ion and atom are initially unpolarized, evaluation of (2.40) using equation (2.34) for \( M(\lambda, \theta) \) gives the same result as Mott and Massey's equation (XIX.53)

\[
\frac{d\sigma}{d\Omega} = \frac{1}{4 (2I+1)} \left\{ I_1 |f^+_{\lambda}(\theta) + f^0_{\lambda}(\theta)|^2 + (I_1+1) |f^0_{\lambda}(\theta) + f^+_{\lambda}(\theta)|^2 \right\} \quad (2.41)
\]

Now that the contribution to \( f^\Theta/\Delta \) as a result...
of charge exchange collisions has been established, it will be utilized in the following chapters to find the time development of the atomic density matrix.
CHAPTER III

TIME DEPENDENCE OF THE DENSITY MATRIX DUE TO CHARGE EXCHANGE COLLISIONS

In the previous chapter the form for the contribution of the time development of the density matrix due to charge exchange collisions was found to have the following form:

\[
\frac{d\rho}{dt} = \frac{\hbar}{i} \left[ i\kappa [P_{\text{ex}}, \rho] + P_{\text{ex}} \rho P_{\text{ex}} - \rho \right]
\]

To this term will now be added the time development of an isolated atom. Assuming for the present that one can ignore all other interactions, one can find the form for the time development of several angular momentum expectation values, specifically \( \langle \hat{s} \rangle \), \( \langle \hat{I}_z \rangle \), \( \langle \hat{I}_y \rangle \), and \( \langle \hat{s} \cdot \hat{I} \rangle \). The assumptions used are the validity of the secular approximation for this problem and the lack of hyperfine coherence in the ground state. The secular approximation, which is discussed in Appendix B, assumes that the time evolution of the density matrix is primarily due to the atomic Hamiltonian. The lack of hyperfine coherence is due to the fact that between collisions there is no term in the Hamiltonian to connect hyperfine states, so they evolve independently of each other and the hyperfine coherence averages to zero. The problem is solved by first transforming to the interaction representation after which one applies the above
two approximations.

Since there are three fundamental angular momenta in this problem, the question arises as to how to combine them. The coupling for the charge exchange collisions is that of combining the two nuclear spins to form a total \( \vec{I} \) and to leave the electron spin \( \vec{S} \) as another variable. However, since the rest of the interactions are either atomic or ionic and the hyperfine interaction is the predominant term in the atomic Hamiltonian, the \( |S_1F_1M_1\rangle \otimes |I_2M_2\rangle \) representation is chosen. By forming the outer product of these states, one can express operators in terms of these basis states. The natural basis for the problem at hand is, however, a linear combination of these outer products, the spherical tensor operators, since when using the new basis, one can conveniently deal with nuclear spins such as \( 3/2 \).

For given angular momenta \( \vec{J} \) and \( \vec{J}' \) with projections \( m \) and \( m' \), the corresponding basis operators are the spherical tensor operators of rank \( \kappa \) and component \( q' \), \( T_{\kappa q}^{(J,J')} \):

\[
T_{\kappa q}^{(J,J')} = \sum_{m,m'} |J \times J'| (-1)^{J-m} \left( \begin{array}{c} m \\ q \\ m' \end{array} \right) \gamma_{2\kappa+1} \quad (3.2)
\]

The normalization of these operators is chosen such that

\[
\mathcal{T} [ T_{\kappa q}^{(J_1,J_2)} (J_3 J_4) ] = \delta_{J_3 J_4} \delta_{J_1 J_3} \delta_{\kappa \kappa} \delta_q q', \quad (3.3)
\]

where

\[
T_{\kappa q}^{(J_3 J_4)} = (-1)^{J_3-J_1-q'} T_{\kappa q}^{(J_1,J_2)} \quad (3.4)
\]
Since both the basis spherical tensor operators and arbitrary spherical tensor operators will be discussed, the following notation will be used:

\( T_{ij}^k (J J') \) is a basis operator of rank \( k \) and component \( q \).

\( T_{ij} (J) \) is an arbitrary operator of rank \( k \) and component \( q \).

Any operator acting in the space spanned by these operators can be expressed in terms of them:

\[
\mathcal{A} = \sum_{J_1, J_2} T_{KQ} (J_1 J_2) A_{KQ} (J_1 J_2) \quad (3.5)
\]

where \( A_{KQ} (J_1 J_2) = \mathcal{A} \langle T_{KQ} (J_1 J_2) \rangle \) by the orthogonality relationship (3.3). More specifically, the atomic density matrix can be given by an expansion in terms of these operators:

\[
\rho_i = \sum_{KQ} \rho_{KQ}^{(FF')} T_{KQ} (FF') \quad (3.5)
\]

where

\[
\rho_{KQ}^{(FF')} (FF') = \langle T_{KQ} (FF') \rangle, \quad T_{KQ}^{(FF')} (FF') = \langle T_{KQ} (FF') \rangle. \quad (3.7)
\]

The ionic density matrix obeys a similar equation in its space. The spin states, therefore, can be described by the multipole polarizations \( \langle T_{KQ} (FF) \rangle \) of the state. When the arguments of the tensor operators are the same, they have a physical interpretation, as can be seen by inspecting table A.1 in Appendix A: \( T_{00} (FF) \) is proportional to the identity operator, \( T_{00} (FF) \) is proportional to the
polarization \( \langle F_{q} \rangle \) and so on. Identities used here for
the spherical tensor operators are also given in Appendix
A with outlines of their proofs.

The fundamental equation that will be used to find
the time development of the various operators and,
therefore, the atomic density matrix is

\[
\frac{d\rho}{dt} = \frac{i}{\hbar} \left[ H_1, \rho \right] + (N_L) \, Tr \rho \left( \frac{d\rho}{dt} \right) \epsilon \epsilon
\]

with \( \left( \frac{d\rho}{dt} \right) \epsilon \epsilon \) given by equation (3.1) and \( N_L \) the
density of ions. Since no observables simultaneously measur­
ing both the atomic and ionic system will be calculated, it
is reasonable to assume that the system density matrix can
be written as

\[
\rho = \rho_a \otimes \rho_i
\]

The average value of an operator acting on the atomic system
only would then be

\[
\langle Q, \rangle = Tr \rho \, Q_1 = \left( Tr \rho \otimes Q \right) \langle Q_1 \rangle
\]

where \( Tr \rho \otimes Q = 1 \).

At this point it is advantageous to remove the time
dependence due to the atomic Hamiltonian by passing to the
interaction representation.
The time development of $\tilde{\rho}$ is then found by inserting (3.11) into equation (3.8). The transformation was defined such that the commutators would cancel yielding

$$\frac{d\tilde{\rho}}{dt} = -\frac{i}{\tau} \left[ \tilde{\rho} - \tilde{\rho}^e - i\mathbf{H}\tilde{\rho}^d \right]$$

(3.12)

where the $\rho$'s are defined as in BHP$^{14}$

$$\rho_i = \tau_{n_2} \rho_{i_2}$$
$$\rho_i^e = \tau_{n_2} \rho_{i_2} \rho_{i_2} P_{i_2}$$
$$\rho_i^d = \tau_{n_2} \left[ P_{i_2}, \rho_{i_2} \right]$$

(3.13a)

with

$$\tilde{\rho}_i = e^{i\mathbf{H}_i \varphi} \rho_i e^{-i\mathbf{H}_i \varphi}$$

(3.13b)

The time constant $\tau$ is given by

$$\frac{1}{\tau} = N_z \sigma_{z} \mathbf{U}_z$$

(3.14)

In order to find the time dependence of various atomic parameters, one must first write equation (3.12) in a form such that it may be easily manipulated. Since the angular momentum involved is the nuclear spin, not the electron spin, it is too difficult to write $P_{i_2}$ in terms
of the nuclear spin operators themselves as can be done in spin exchange theory, a spin one-half system. For this reason, \( P_{Ex} \) will be expressed in terms of the spherical tensor operators.

Recall that the exchange operator \( P_{Ex} \) is defined as

\[
P_{Ex} = P_S - P_A
\]  

This can be written as

\[
P_{Ex} = \sum_{I_{odd}} \sum_{m_z}^{I} |IM><IM| - \sum_{I_{even}} \sum_{m_z=I}^{I} |IM><IM|
\]  

where \( \hat{I} = \hat{I}_I + \hat{I}_L \).

This can be rewritten in terms of the \( T_{ij} \) as

(\text{using A.13})

\[
P_{Ex} = \frac{1}{2} \sum_{IM} \left[ 1 - (-1)^I \right] |IM><IM| - \frac{1}{2} \sum_{IM} \left[ 1 + (-1)^I \right] |IM><IM| 
\]

\[
= -\sum_{IM} (-1)^I |IM><IM|
\]

\[
= -\sum_{I} (-1)^I \sqrt{2I+1} \ T_{00} (II)
\]

Note that the electron spin has been suppressed in the derivation of the charge exchange operator as charge exchange collisions do not immediately affect the electron spin. It can now be included in terms of the electron spin identity matrix:

\[
P_{Ex} = I(s) \otimes (P_s - P_A)
\]

\[
= -\sum_{I} (-1)^I \sqrt{(2I+1)(2s+1)} \ T_{00} (ss) \ T_{00} (II)
\]
Equation (3.18) is not in the correct coupling scheme for the problem at hand. Therefore, $T_{00}^{(II)}$ must be expanded in terms of its constituent nuclear spins $I$, and $I_z$ and then terms in $I$, and $S$ recombined to yield $P_{Ex}^I$ in terms of $T_{KQ}^{(EF')} \text{ and } T_{K'Q'}^{(I_zI_z)}$. From equation (A.17) in Appendix A, $T_{00}^{(II)}$ can be expressed as a product of tensor operators for the two individual $I$'s as

$$ T_{00}^{(II)} = \sum_{L, q, \ell} T_{L, q, \ell}^{(I, I_z)} \overline{T}_{L, q, \ell}^{(I_z, I)} \frac{\gamma (2I+1)^2 (2I_z+1)(2\ell +1)}{2\ell +1} \times$$

$$ \times \begin{pmatrix} L, L_z, 0 \\ \ell, \ell_z, 0 \end{pmatrix} \begin{bmatrix} L, L_z, 0 \\ I, I_z, I \\ I, I_z, I \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix}$$

The 3-J and 9-J symbols can be evaluated by means of (A.12) and (A.34) to give

$$ T_{00}^{(II)} = (-)^{I_z + I_z + I} \sum_{L, q} (-)^q T_{L, q}^{(I, I_z)} \overline{T}_{L, q}^{(I_z, I)} \frac{\gamma (2I+1)^2 (2I_z+1)(2\ell +1)}{2\ell +1} \times$$

$$ \times \begin{pmatrix} I, I_z, I \\ I_2, I, \ell \end{pmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix}$$

By inserting (3.20) into (3.18) one finds (noting that since $I_1 = I_2 = \frac{\text{ODD INTEGER}}{2}$, $(-)^{I_z + I_z + I} = 1$):

$$ P_{Ex}^I = \sum_{L, q} (-)^q \overline{T}_{L, q}^{(SS)} \overline{T}_{L, q}^{(I, I_z)} \frac{\gamma (2S+1)(2I+1)}{2I+1} \begin{pmatrix} I, I_z, I \\ I_2, I, \ell \end{pmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix}$$

$$ \times \begin{pmatrix} I, I_z, I \\ I_2, I, \ell \end{pmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix} \begin{bmatrix} I, I_z, I \\ I_2, I, \ell \end{bmatrix}$$

The sum over $\overline{I}$ can be immediately performed by means of (A.35):
The atomic part of (3.22) can be reexpressed by means of (A.18)

\[
T_{00}(SS) T_{kq} (I,I,) = \sum_{KQ} (-1)^{[F'K-F]+[Q]} T_{(2F+1)(2F'+1)(2K+1)(2K'+1)} \times
\]
\[
\begin{pmatrix}
0 & h & 0 \\
0 & q & -Q \\
S & I & F'
\end{pmatrix}
\begin{pmatrix}
0 & h & K \\
S & I & F
\end{pmatrix}
\]

(3.23)

Again with the aid of (A.12) and (A.34) one can write

\[
T_{00}(SS) T_{kq} (I,I,) = \sum_{FF'} (-1)^{F+I_{1}+S+\zeta} T_{kq} (F,F') \times
\]
\[
\sqrt{\frac{(2F+1)(2F'+1)}{(2S+1)}}
\begin{pmatrix}
I & F & S \\
F' & I & \zeta
\end{pmatrix}
\]

(3.24)

The exchange operator can now be written in terms of atomic and ionic coordinates as

\[
P_{Ex} = \sum_{kq} (-1)^{[F+I_{1}+S+\zeta]+[Q]} T_{kq} (F,F') T_{h-q} (I_{2}I_{2}) \times
\]
\[
\sqrt{\frac{(2F+1)(2F'+1)}{(2S+1)}}
\begin{pmatrix}
I & F & S \\
F' & I & \zeta
\end{pmatrix}
\]

(3.25)
or

$$
\rho_{Fx} = \sum_{k<q} (-)^{k} T_{k}^{(Ff')} T_{k-\frac{1}{2}}^{(I_{2}I_{2})} P_{Fx}^{(Ff'); k}\tag{3.26}
$$

with

$$
P_{Fx}^{(Ff'); k} = (-)^{F+I_{2}+S+I} \sqrt{\frac{(2F+1)(2F'+1)}{2}} \left\{ \begin{array}{c} I_{2}, F, S \\ F', I_{2}, k \end{array} \right\} \tag{3.27}
$$

Equation (3.26) for $\rho_{Fx}$ can now be used in equations (3.13) to evaluate the various contributions of the members of the charge exchange term.

First consider $\rho_{i}^{d}$:

$$
\rho_{i}^{d} = T_{n_{2}} [ P_{Fx}, \rho_{z} ] \tag{3.28}
$$

Inserting (3.26) into (3.28), one finds

$$
\rho_{i}^{d} = \sum_{k<q} (-)^{k} P_{Fx}^{(Ff'); k} T_{n_{2}} [ T_{k}^{(Ff')} T_{k-\frac{1}{2}}^{(I_{2}I_{2})}, \rho_{z} ] \tag{3.29}
$$

Recalling (3.9) and (3.10), one can now write $\rho_{i}^{d}$ as

$$
\rho_{i}^{d} = \sum_{k<q} (-)^{k} P_{Fx}^{(Ff'); k} \langle T_{k-\frac{1}{2}}^{(I_{2}I_{2})} \rangle [ T_{k}^{(Ff')}, \rho_{i} ] \tag{3.30}
$$

Next consider $\rho_{i}^{c}$:

$$
\rho_{i}^{c} = T_{n_{2}} P_{Fx} \rho_{z} P_{Fx} \tag{3.31}
$$
Now inserting (3.26) into (3.31) one finds
\[
\rho^e_i = \sum_{kq, \ell' m} (-1)^{q+m} \rho_{kq} (F'F', \ell') \rho_{\ell m} (F''F'', \ell) \times \\
\times T_{qI_i} \left[ T_{kq} (F'F') T_{k-q} (I_i I_i) \rho_{i2} T_{\ell' m} (F''F'') T_{\ell' -m} (I_i I_i) \right]
\]
By using the property of the trace that \( T_{nABC} = T_{nCAB} \), (3.32) becomes
\[
\rho^e_i = \sum_{kq, \ell' m} (-1)^{q+m} \rho_{kq} (F'F', \ell') \rho_{\ell m} (F''F'', \ell) \times \\
\times T_{kq} (F'F') \rho_{i2} T_{\ell' m} (F''F'') \left( T_{\ell' -m} (I_i I_i) T_{k-q} (I_i I_i) \right)
\]
Equations (3.30) and (3.33) give the general forms to be used in (3.12) in conjunction with (3.13b) for the effect of charge exchange collisions on the atomic density matrix.

1. Ionic Density Matrix

Now make the assumption that the polarization and all higher multipole moments of the ion may be kept zero experimentally. In that case, only the \( \langle T_{00} (I_i I_i) \rangle \) term is non-zero. Since \( T_n \rho_2 = 1 \),
\[
\rho_2 = \frac{1}{\sqrt{2I_i + 1}} T_{00} (I_i I_i)
\]
and
\[
\langle T_{kq} (I_i I_i) \rangle = \frac{1}{\sqrt{2I_i + 1}} \delta_{k0} \delta_{q0}
\]
As a result of this assumption, which is the same assumption made by Grossetête\(^{20} \) in her spin exchange analysis, \( \rho_i^d \)
vanishes. This can be seen by inspection of (3.30). Since \( \mathcal{L} = 0 \) and \( \mathcal{Q} = 0 \).

\[
\left[ T_{\mathcal{L} \mathcal{Q}}(FF'), \rho_1 \right] = \frac{1}{\sqrt{2I_z+1}} \delta_{FF'} \left[ I(\mathcal{L}), \rho_1 \right] = 0
\]  

(3.36)

To find \( \rho_1^e \) under this assumption, one must reexpress \( \langle T_{\mathcal{L} \mathcal{Q}}(I_z I_z) \rangle \) in terms of a sum of \( T_{\mathcal{L} \mathcal{Q}} \)'s by means of (A.15) and pick out the \( T_{00}(I_z I_z) \) term:

\[
\langle T_{\mathcal{L} \mathcal{Q}}(I_z I_z) \rangle = \sum_{kQ} (-)^{[2I_z] + [\mathcal{Q}]} \langle T_{\mathcal{L} \mathcal{Q}}(I_z I_z) \rangle \times
\]

\[
\times \sqrt{2\mathcal{L}+1)(2\mathcal{L}+1)(2\mathcal{Q}+1)} \begin{pmatrix} \ell & \mathcal{L} & k \\ m & q & \mathcal{Q} \end{pmatrix} \begin{pmatrix} \ell & \mathcal{L} & k \\ m & q & \mathcal{Q} \end{pmatrix}
\]

But from (3.35)

\[
\langle T_{\mathcal{L} \mathcal{Q}}(I_z I_z) \rangle = \frac{1}{\sqrt{2I_z+1}} \delta_{\mathcal{L}0} \delta_{\mathcal{Q}0}
\]

So

\[
\langle T_{\mathcal{L} \mathcal{Q}}(I_z I_z) \rangle = \sqrt{2\mathcal{L}+1)(2\mathcal{L}+1)} (-)^{[2I_z]} \times
\]

\[
\times \begin{pmatrix} \ell & \mathcal{L} & 0 \\ m & q & 0 \end{pmatrix} \begin{pmatrix} \ell & \mathcal{L} & 0 \\ m & q & 0 \end{pmatrix}
\]

The 3-J symbol is given by (A.12) and the 6-J symbol by (A.33). Using these values, one finds

\[
\langle T_{\mathcal{L} \mathcal{Q}}(I_z I_z) \rangle = (-)^{\mathcal{Q}} \delta_{\mathcal{L}k} \delta_{\mathcal{Q}m} \frac{1}{2I_z+1} \]

(3.39)
Therefore, using (3.39) in (3.33) \( \rho_i^e \) becomes
\[
\rho_i^e = \sum_{k} \sum_{F,F'} (-)^k \rho_{Fx}(F; \ell) \rho_{Fx}(F'; \ell) \times \\
\times T_k q (F,F') \rho_i \ T_{k-q}(F'',F''')
\]
(3.40)
The result is that in this approximation,
\[
\frac{d\rho_i^e}{dt} = -\frac{i}{\epsilon} [\rho_i^e, \rho_i^e]
\]
(3.41)
with \( \rho_i^e = e^{i \mathcal{H}_i t} \rho_i e^{-i \mathcal{H}_i t} \) and \( \rho_i^e \) given by (3.40). Taking matrix elements of (3.41), one finds
\[
\frac{d}{dt} <FM|\rho_i|F'M'> = -\frac{i}{\epsilon} \left\{ <FM|\rho_i|F'M'> - \sum_{F''F'''} \sum_{k} \left[ \frac{\epsilon^{M'T_k q (F''')/\epsilon^{F'''} - \epsilon^{F''}}}{2i, + 1} \right] \times \\
\times T_k q (F,F') \rho_i (F,F''') T_{k-q}(F'',F''') \right\}
\]
(3.42)
Equation (3.42) is the general form for the development of a matrix element of the atomic density matrix in the interaction representation due to charge exchange collisions.

2. Atomic Density Matrix -
Application of the Secular Approximation

In the secular approximation it is assumed that since \( E_{F'M'} \gg \frac{1}{\epsilon} \) the primary time dependence of \( <FM|\rho_i|F'M'> \) is \( e^{\epsilon^{F'M'}t} \). This implies that the primary variation of \( <FM|\rho_i|F'M'> \) is due to the nonoscillatory terms on the right. This in turn implies that the exponential
term must be unity:

\[ E_{F'''} - E_{F'''} = E_{F''''} - E_{F''''} \]  

(3.43)

Therefore, putting (3.43) into (3.42):

\[
\frac{d\langle FM| \tilde{\rho}_i| F'M'\rangle}{dt} = -\frac{i}{\hbar} \left\{ \langle FM| \tilde{\rho}_i| F'M'\rangle - \frac{\sum_{F''''''=F'''''} (E_{F''''''} - E_{F'''''}) E_{F''''''}^*}{2\hbar + 1} \times \langle F''''''| T_{k-q} (FF'')| F'M'\rangle \right\} 
\]

(3.44)

Upon transformation back to the Schrödinger picture, equation (3.44) becomes

\[
\frac{d\langle FM| \rho_i| F'M'\rangle}{dt} = -i \left\{ \mathcal{H}_i, \rho_i \right\} - \frac{i}{\hbar} \left\{ \langle FM| \rho_i| F'M'\rangle - \frac{\sum_{F''''''=F'''''} (E_{F''''''} - E_{F'''''}) E_{F''''''}^*}{2\hbar + 1} \times \langle F''''''| T_{k-q} (FF'')| F'M'\rangle \right\} 
\]

(3.45)

The restriction is the same in either picture, and

\[
\langle FM| \rho_i^e| F'M'\rangle = \frac{\sum_{F''''''=F'''''} (E_{F''''''} - E_{F'''''}) E_{F''''''}^*}{2\hbar + 1} \times \langle F''''''| T_{k-q} (F''')| F'M'\rangle 
\]

(3.46)
The exponential is missing due to the secular approximation. In order to use equation (3.46), the matrix elements must be evaluated according to (3.2) and the $\mathcal{R}_x(F,F',L)$ explicitly expressed according to (3.27).

\[
\langle F m | \rho | F' m' \rangle = \sum_{E'' E' = E - E'} \frac{(-1)^{E'' - E'}}{(2I + 1)} \langle F'' m'' | \rho | F'' m'' \rangle \times 
\]

\[
\times \left[ (-1)^{F - m} \left( F, \ell, I \right) \left( \frac{2I + 1}{2I} \right) \right] \left[ (-1)^{-m''} \left( -m', I \right) \left( \frac{2I + 1}{2I} \right) \right] \sqrt{2I + 1} \right] \times 
\]

\[
\times \left[ (-1)^{F + I + S + L} \left( \frac{1}{2I + 1} \right) \left( F', I, L \right) \right] \left[ (-1)^{F' + I + S + L} \left( \frac{1}{2I + 1} \right) \left( F', I, L \right) \right] \right] \times 
\]

\[
\left( 3.47 \right) 
\]

Since $I_1$ and $S$ are both half integral, the combination $I_1 + S$ is an integer and the total phase factor can thus be written, using the notation of Appendix A, page 93,

\[
\phi = \left[ \delta \right] + \left[ F - m \right] + \left[ F'' - m'' \right] + \left[ F' \right] + \left[ I_1 + S \right] + \left[ L \right] + 
\]

\[
+ \left[ F'' \right] + \left[ I_1, + S \right] + \left[ L \right] 
\]

\[
= \delta + m + m'' 
\]

At this point no further reduction of (3.47) can be made. Rewritten, it is

\[
\langle F m | \rho | F' m' \rangle = \sum_{E'' E' = E - E'} \frac{(-1)^{\delta + m + m''}}{(2I + 1)} \langle F'' m'' | \rho | F'' m'' \rangle \times 
\]

\[
\times \sqrt{2I + 1} \left( F, \ell, I \right) \left( \frac{2I + 1}{2I} \right) \left( F', I, L \right) \left( \frac{2I + 1}{2I} \right) \right] \times 
\]

\[
\times \sqrt{2I + 1} \left( F, \ell, I \right) \left( \frac{2I + 1}{2I} \right) \left( F', I, L \right) \left( \frac{2I + 1}{2I} \right) \right] \times 
\]

\[
\times \left[ (-1)^{-m''} \left( -m', I \right) \left( \frac{2I + 1}{2I} \right) \right] \times 
\]

\[
\left( 3.49 \right) 
\]
3. **Time Development of $\langle T_q(k)\rangle_F$**

Since the charge exchange operator is independent of the axis of orientation, partial traces over $\mathcal{M}$ can be performed easily. As a result consider the time dependence of the following arbitrary spherical tensor atomic operator

$$\langle T_q(k) \rangle_F = \sum_M \langle F'M \mid \rho, T_q(k) \mid F'M \rangle \hspace{1cm} (3.50)$$

Similarly define

$$\langle T_q(k) \rangle_F^e = \sum_M \langle F'M \mid \rho^e, T_q(k) \mid F'M \rangle \hspace{1cm} (3.51)$$

By inserting a complete set of states in (3.51) and using the Wigner-Eckart theorem (A.5) one finds

$$\langle T_q(k) \rangle_F^e = \sum_{F'M'} (-)^{F'M'} \left( \begin{array}{ccc} F' & K & F \\ -m' & Q & m \end{array} \right) \langle F', \|T(k)\|F \rangle \hspace{1cm} (3.52)$$

Equation (3.49) may be inserted into (3.52) to give

$$\langle T_q(k) \rangle_F^e = \sum_{F',F''} \left( \begin{array}{ccc} F' & F'' & F \\ \|T(k)\| & |F \rangle \langle F'\| \right) \frac{(-)^{F'}}{2I^F} \frac{1}{\sqrt{(2F'')(2F'+1)(2F''+1)(2F'''+1)}} \times$$

$$\times \sum_{m''} (-)^{m''} \langle F''m'' \mid \rho, F''m'' \rangle \sum_{I} (2I+1) \left\{ \begin{array}{ccc} F' & I & S \\ I, F'' & \end{array} \right\} \left\{ \begin{array}{ccc} F'' & I & S \\ I, F' & \end{array} \right\} \times$$

$$\times \sum_{m} (-)^{I+m'+m} \left( \begin{array}{ccc} F' & K & F \\ -m' & Q & m \end{array} \right) \left( \begin{array}{ccc} F & I & F'' \\ -m' & Q & m'' \end{array} \right) \left( \begin{array}{ccc} F'' & I & F \\ -m'' & q & m' \end{array} \right)$$
Define the following sum which incorporates all the phase factors and 3-J symbols in (3.53)

\[
S = (-1)^{F' + N''} \sum_{\varphi} (-1)^{q + m + m'} \left( \begin{array}{ccc} F' & K & F \\ F & L & F'' \end{array} \right) \left( \begin{array}{ccc} F'' & L & F' \end{array} \right)
\]

(3.54)

Since \( q, m \) and \( m' \) are just dummy summation variables, change the sign on all three and permute the first 3-J symbol:

\[
S = (-1)^{F'' + m'' + K + L} \sum_{\varphi} (-1)^{q + m + m'} \left( \begin{array}{ccc} F & K & F' \\ -m & Q & m' \\ m & -q & m'' \end{array} \right) \left( \begin{array}{ccc} F'' & L & F' \end{array} \right)
\]

(3.55)

The sum \( S \) is now in a form where (A.16) can be used to give

\[
S = (-1)^{F'' + m'' + K + L} \left( \begin{array}{ccc} F'' & K & F'' \\ -m'' & Q & m'' \end{array} \right) \left\{ \begin{array}{ccc} F'' & K & F' \\ F & I & F' \end{array} \right\}
\]

(3.56)

Upon replacing the sum \( S \) into (3.53) one has

\[
\langle T_0(K)_{F'}^C = \sum_{F,F''} \langle F' F'' | T(K) | F \rangle \sqrt{(2F+1)(2F'+1)(2F''+1)} \]

* \[ \begin{array}{c} \sum_{m,m''} \langle F'' M' | \rho | F'' M'' \rangle (-1)^{F' + K + m''} \left( \begin{array}{ccc} F'' & K & F'' \\ -m'' & Q & m'' \end{array} \right) \]

(3.57)

* \[ \sum_{\mathcal{L}} (-1)^{\mathcal{L}(2\mathcal{L}+1)} \left\{ \begin{array}{ccc} F & I & S \\ I & F & S \end{array} \right\} \left\{ \begin{array}{ccc} F'' & I & S \\ I & F' & S \end{array} \right\} \left\{ \begin{array}{ccc} F'' & K & F'' \\ F & I & F' \end{array} \right\}
\]

The sum over \( \mathcal{L} \) can immediately be performed by using (A.36).
\[ S' = \sum_{L} (-1)^{L} (2L+1) \left\{ F \mid I, S \right\} \left\{ F'' \mid I, S \right\} \left\{ F''' \mid K, F'' \right\} \]

\[ = \sum_{L} (-1)^{L} (2L+1) \left\{ F \mid I, S \right\} \left\{ F'' \mid K, F'' \right\} \left\{ I, F' \right\} \left\{ F \mid I, S \right\} \]

\[ = (-) \left\{ K+F''+I+F'+F'''+S+F+S+I, F \mid I, S \right\} \left\{ S \mid K, S \right\} \left\{ I, S \right\} \left\{ F, I, F \right\} \]

The phase factor can be reduced by noting that since \( I, \) and \( S \) are half integral, then \( I+S \) must be an integer so \((-)^{2(I+S)} \neq 1\).

As a result one can write \( S' \) as

\[ S' = (-)^{K+F''+F'+F'''+F} \left\{ K \mid F'', F''' \right\} \left\{ S \mid K, S \right\} \left\{ I, S \right\} \left\{ F', I, F \right\} \]

and inserting this back into \((3.57)\), one finds

\[ \langle T_{\nu}(\kappa) \rangle_F = \sum_{F'''} \langle F' \mid T(\kappa) \mid F \rangle \left\{ F'' \mid 2L+1 \right\} \left\{ (2L+1)(2F''+1)(2F'''+1) \right\} \times \]

\[ \ast \left( F+I \right) \left\{ K \mid F', F''' \right\} \left\{ S \mid K, S \right\} \left\{ I, S \right\} \left\{ F', I, F \right\} \]

\[ \ast \sum_{m'''} \langle F'''' \mid \rho, F''' \rangle \langle F''' \mid \rho'''' \rangle (-)^{-m'''} \left\{ F'''' \mid K, F'' \right\} \left\{ -m'''' \mid \rho, m'''' \right\} \]

By recalling from Chapter I, equation (1.7), that the energy levels are linear in \( m \) and by inspection of equations (3.52) and (3.60) one sees that the secular approximation is automatically satisfied as far as the \( m \) dependence and the restriction is really on the \( F' S \).
By choosing specific $T_q(k)$'s one can derive their time dependence in terms of equation (3.60). The equation that these observables must obey is, from (3.50)

$$\frac{d}{dt} \langle T_q(k) \rangle_{F} = \sum_{M} \langle F M | \frac{\partial}{\partial t} T_q(k) | FM \rangle$$

(3.61)

Before deriving the time development of a tensor operator from equation (3.61), one must make one more assumption, that of no hyperfine coherence. This is the same assumption that Gross et al. uses for spin exchange collisions. Mathematically, this means that

$$\langle F^{'M''} | \rho | F^{'M'} \rangle = \delta_{F^{'M''}, F^{'M'}} \langle F^{'M''} | \rho | F^{'M'} \rangle$$

(3.62)

Due to the secular approximation this immediately implies that

$$F = F'$$

(3.63)

Physically, it means that different hyperfine states evolve independently of each other between charge exchange collisions. Under this approximation, the defining relationships for the expectation values (3.50) and (3.51) can be written

$$\langle T_q(k) \rangle_{F} = \sum_{m,m'} \langle FM | \rho | FM' \rangle \langle FM' | T_q(k) | FM \rangle$$

(3.64)

and

$$\langle T_q(k) \rangle^{c}_{F} = \sum_{M,M'} \langle FM | \rho^{c} | FM' \rangle \langle FM' | T_q(k) | FM \rangle$$

(3.65)
Under this approximation one may also rewrite (3.60) as

\[ \langle T_q(k) \rangle_F^c = \langle F \| T(k) \| F \rangle \left( \frac{2F+1}{2I_1+1} \right) (-)^F \left\{ \begin{array}{c} S \leq S' \\ F \leq I, F \end{array} \right\} * \]

\[ \times \sum_{F'} (-1)^{F''(2F''+1)} \left\{ \begin{array}{c} K \leq F'' \\ F'' \leq S'' \end{array} \right\} \sum_{m''} \langle F'' m'' | \rho | F'' m'' \rangle \]

\[ \times \langle F'' m'' | T_q(k) | F'' m'' \rangle \frac{1}{\langle F'' \| T(k) \| F'' \rangle} \]

where the Wigner-Eckart theorem (A.5) was used on the 3-J symbol. By recalling (3.64) one can see that the sum over \( m", m'' \) can be replaced by \( \langle T_q(k) \rangle_{F''} \). Therefore (3.66) becomes

\[ \langle T_q(k) \rangle_F^c = \langle F \| T(k) \| F \rangle \left( \frac{2F+1}{2I_1+1} \right) \left\{ \begin{array}{c} S \leq F \leq I, \\ F \leq S \leq K \end{array} \right\} * \]

\[ \times \sum_{F'} (-1)^{F''(2F''+1)} \left\{ \begin{array}{c} S \leq F'' \leq I, \\ F'' \leq S \leq K \end{array} \right\} \frac{\langle T_q(k) \rangle_{F''}}{\langle F'' \| T(k) \| F'' \rangle} \]

Recalling equation (1.6) from Chapter I,

\[ H = A \bar{T} \cdot \bar{S} - \mu_0 g_F H_o F_z \]  

(3.61) can be rewritten as

\[ \frac{d}{dt} \langle T_q(k) \rangle_F = -i \mu_0 g_F H_o Q \langle T_q(k) \rangle_F - \]

\[ - \frac{1}{\hbar} \left[ \langle T_q(k) \rangle_F - \langle T_q(k) \rangle_F^c \right] \]

Consider first the case of \( K=0 \) and \( Q=0 \). Equation (3.67) becomes in this case
\[ \langle T_0(o) \rangle_F^e = \langle F || T(o) || F \rangle (-)^F \frac{(2F+1)}{(2I_1+1)} \left( \frac{S}{F} \frac{F}{S} \frac{I_1}{O} \right) \times \]
\[ \times \sum_{F''} (-)^{F''} (2F''+1) \left( \frac{S}{F''} \frac{F''}{S''} \frac{I_1}{O} \right) \frac{\langle T_0(o) \rangle_{F''}}{\langle F'' || T(o) || F'' \rangle} \]

(3.70)

One can evaluate the $G-J$ symbol from (A.33). The result is

\[ \langle T_0(o) \rangle_F^e = \langle F || T(o) || F \rangle \frac{\sqrt{2F+1}}{(2I_1+1)(2S+1)} \]

(3.71)

Two obvious choices for $T_0(o)$ are $\mathcal{I}(F)$ and $\mathcal{I}_i \cdot \mathcal{S}$. Recall the definition of $\mathcal{I}(F)$ (A.13):

\[ \mathcal{I}(F) = \sqrt{2F+1} T_{oo}(F,F) \]

(3.72)

Using equation (3.71) one finds that the exchange hyperfine populations are given by

\[ (\sigma_F^e)^e = \frac{2F+1}{(2I_1+1)(2S+1)} \]

(3.73)

where $\langle F || \mathcal{I} || F \rangle = \sqrt{2F+1}$. $(\sigma_F^e)^e$ is seen to be the equilibrium value of the hyperfine populations, as expected, since charge exchange collisions tend to disorient the atoms.

Again using (3.71) one can find the average value of the operator $\mathcal{I}_i \cdot \mathcal{S}$ due to exchange:

\[ \langle \mathcal{I}_i \cdot \mathcal{S} \rangle_F^e = \frac{(2F+1)}{(2I_1+1)(2S+1)} \cdot \frac{1}{2} \left[ F(F+1)-I_i(I_i+1)-S(S+1) \right] \]

(3.74)
where \( \langle F \parallel \mathbf{F} \parallel F \rangle = \frac{1}{2} \left[ F(F+1) - (I_x I_x + I_y I_y + I_z I_z) - S(S+1) \right] \frac{1}{2F+1} \).

Since one can find the exchange term for any zeroth rank tensor, the time development of this tensor can immediately be found from (3.69) and the initial conditions. Specifically

\[
\frac{d}{dt} \langle T_0(0) \rangle_F = -\frac{1}{\tau} \left[ \langle T_0(0) \rangle_F - \langle T_0(0) \rangle^e_F \right] \tag{3.75}
\]

But from equation (3.71) \( \langle T_0(0) \rangle^e_F \) is a constant, so the general form for the time development of \( \langle T_0(0) \rangle_F \) is

\[
\frac{d}{dt} \langle T_0(0) \rangle_F = -\frac{1}{\tau} \left[ \langle T_0(0) \rangle_F - \gamma_F \right] \tag{3.76}
\]

The solution of this equation is

\[
\langle T_0(0) \rangle_F = \gamma_F + \beta_F e^{-t/\tau} \tag{3.77}
\]

with \( \beta_F \) given by initial conditions. Equation (3.77) states that under the influence of charge exchange collisions alone the expectation value of any zeroth rank tensor operator decays with one time constant which is independent of the specific hyperfine level chosen. If one sums equation (3.77) over all hyperfine levels, one can say that the overall expectation value behaves in the same fashion. Note that this agrees with the two specific cases given by Grossetête\(^{20}\) for electron spin exchange collisions.
Now consider an operator \( S_q(k) \) that is a tensor operator of rank \( k \) and component \( Q \) acting only in \( S \) space. From (A.29) its reduced matrix element is

\[
\langle F || S(k) || F \rangle = (-)^{S+I+F+k} \frac{(2F+1)}{(2I+1)} \left\{ \begin{array}{c} S \in I, \\ F \leq k \end{array} \right\} \langle S || S(k) || S \rangle \quad (3.78)
\]

Upon insertion of (3.78) into (3.67), one finds that \( \langle S_q(k) \rangle \) is proportional to the total value of \( \langle S_q(k) \rangle \) not just the value for a specific \( F \).

\[
\langle S_q(k) \rangle \propto (-)^{S+I+F+k} \frac{(2F+1)}{(2I+1)} \left\{ \begin{array}{c} S \in I, \\ F \leq k \end{array} \right\} \langle S_q(k) \rangle \quad (3.79)
\]

Upon performing the obvious cancellations, one finds

\[
\langle S_q(k) \rangle = \frac{(2F+1)}{(2I+1)} \left\{ \begin{array}{c} S \in I, \\ F \leq k \end{array} \right\} \langle S_q(k) \rangle \quad (3.80)
\]

The differential equation for the time development of \( \langle S_q(k) \rangle \) then becomes

\[
\frac{d}{dt} \langle S_q(k) \rangle = \left[ -i\Delta E_p H_0 Q - \frac{1}{c} \right] \langle S_q(k) \rangle + \frac{1}{c} \frac{(2F+1)}{(2I+1)} \left\{ \begin{array}{c} S \in I, \\ F \leq k \end{array} \right\} \langle S_q(k) \rangle \quad (3.81)
\]

Since \( \tilde{g}_q \) in the first term of (3.81) possesses a complicated \( F \) dependence, consider the case for \( Q = 0 \).
To solve this first sum over all \( F \) to find the time dependence of \( \langle S_0(k) \rangle \). Then use that value in (3.81) to see how the individual \( \langle S_0(k) \rangle_F \)'s behave.

\[
\frac{d}{dt} \langle S_0(k) \rangle = -\frac{i}{\tau} \left[ 1 - \sum_F \frac{(2F+1)^2}{(2\Sigma F+1)} \left\{ \frac{S F \uparrow \downarrow}{F S K} \right\}^2 \right] \langle S_0(k) \rangle \tag{3.82}
\]

Upon integration this yields

\[
\langle S_0(k) \rangle = \langle S_0(k) \rangle_{t=0} e^{-\frac{t}{\tau_K}} \tag{3.83}
\]

where

\[
\frac{1}{\tau_K} = \frac{1}{\tau} \left[ 1 - \sum_F \frac{(2F+1)^2}{(2\Sigma F+1)} \left\{ \frac{S F \uparrow \downarrow}{F S K} \right\}^2 \right] \tag{3.84}
\]

The equation for \( \langle S_0(k) \rangle_F \) is then

\[
\frac{d}{dt} \langle S_0(k) \rangle_F = -\frac{i}{\tau} \langle S_0(k) \rangle_F + \frac{1}{\tau} \frac{(2F+1)^2}{(2\Sigma F+1)} \left\{ S F \uparrow \downarrow \right\}^2 \langle S_0(k) \rangle_{t=0} e^{-\frac{t}{\tau_K}} \tag{3.85}
\]

The solution to (3.85) can be found by regrouping the equation and integrating.

\[
\frac{d}{dt} \left[ e^{\frac{t}{\tau_K}} \langle S_0(k) \rangle_F \right] = \frac{1}{\tau} \frac{(2F+1)^2}{(2\Sigma F+1)} \left\{ S F \uparrow \downarrow \right\}^2 \langle S_0(k) \rangle_{t=0} e^{-\frac{t}{\tau_K}} \tag{3.86}
\]

which gives, upon integration

\[
\langle S_0(k) \rangle_F = e^{-\frac{t}{\tau_K}} \left[ \langle S_0(k) \rangle_F_{t=0} + \frac{1}{\tau} \frac{(2F+1)^2}{(2\Sigma F+1)} \left\{ S F \uparrow \downarrow \right\}^2 \right] \tag{3.87}
\]
\[ \frac{1}{i \frac{t}{\tau} + \frac{1}{\tau}} \langle S_0(k) \rangle_{t=0} \left( e^{-i \frac{t}{\tau} \left( \frac{1}{\tau} - \frac{1}{\tau} \right)} - 1 \right) \]

or, multiplying through by the factor in front

\[ \langle S_0(k) \rangle_t = e^{\frac{-t}{\tau}} \left[ \langle S_0(k) \rangle_{t=0} - \frac{(2F+1)^2 \left\{ S F I \right\}^2}{\sum_{F'} (2F'+1)^2 \left\{ S F' I \right\}^2} \langle S_0(k) \rangle_{t=0} \right] + \]

\[ + 2 e^{\frac{-t}{\tau}} \left[ \langle S_0(k) \rangle_{t=0} \frac{(2F+1)^2 \left\{ S F I \right\}^2}{\sum_{F'} (2F'+1)^2 \left\{ S F' I \right\}^2} \right] \]

For \( Q \neq 0 \) one must again employ the secular approximation. Recall equation (3.81) for \( \langle S_Q(k) \rangle_t \)

\[ \frac{d}{dt} \langle S_Q(k) \rangle_t = -i \omega_{FQ} t \langle S_Q(k) \rangle_t + \frac{1}{\tau} \alpha_{FK} \langle S_Q(k) \rangle_t \]

where

\[ \omega_{FQ} = \mu_0 g_F H_0 Q \]

and

\[ \alpha_{FK} = \frac{(2F+1)^2}{(2F'+1)^2} \left\{ S F I \right\}^2 \]

Since \( t/\tau < \omega_{FQ} \), the primary time dependence of \( \langle S_Q(k) \rangle_t \)

is due to the oscillation from the Zeeman term. Remove this dependence by setting

\[ \langle S_Q(k) \rangle_t = e^{-i \omega_{FQ} t} \langle S_Q(k) \rangle' \]

Then by putting (3.90) into (3.81), one finds that \( \langle S_Q(k) \rangle'_{t=0} \)
obeys

\[
\frac{d}{dt} \langle S_q(k) \rangle'_F = -\frac{i}{c} \langle S_q(k) \rangle'_F + \frac{\alpha_{Fk}}{c} e^{i \omega_{Fk} t} \langle S_q(k) \rangle 
\] (3.91)

Since

\[
\langle S_q(k) \rangle = \sum_{F'} \langle S_q(k) \rangle'_{F'} = \sum_{F'} e^{-i \omega_{F'} q t} \langle S_q(k) \rangle'_{F'} 
\] (3.92)

one can write (3.91) as

\[
\frac{d}{dt} \langle S_q(k) \rangle'_F = -\frac{i}{c} (1 - \alpha_{Fk}) \langle S_q(k) \rangle'_F + \frac{\alpha_{Fk}}{c} \sum_{F' \neq F} \langle S_q(k) \rangle'_{F'} e^{i (\omega_{Fq} - \omega_{F0}) t} 
\] (3.93)

The \( F' = F \) term in the sum has been specifically extracted because it will be shown that the contribution of the remaining sum is negligible. Equation (3.93) can be solved by iteration and with this in mind, rewritten as

\[
\frac{d}{dt} \left[ e^{\frac{i}{c} (1 - \alpha_{Fk}) t} \langle S_q(k) \rangle'_F \right] = \frac{\alpha_{Fk}}{c} \sum_{F' \neq F} \langle S_q(k) \rangle'_{F'} e^{-i (\omega_{Fq} - \omega_{F0}) t + \frac{i}{c} (1 - \alpha_{Fk}) t} \] (3.94)

Equation (3.94) can be integrated to give

\[
\langle S_q(k) \rangle'_F = e^{-\frac{i}{c} (1 - \alpha_{Fk}) t} \left[ \langle S_q(k) \rangle'_{F'} \right]_{t=0} + \frac{\alpha_{Fk}}{c} \sum_{F' \neq F} \int_0^t d t' e^{-i (\omega_{Fq} - \omega_{F0}) t' + \frac{i}{c} (1 - \alpha_{Fk}) t'} \langle S_q(k) \rangle'_{F'} \right] 
\] (3.95)
One iteration of equation (3.95) gives

\[
\langle S_Q(k) \rangle_F = e^{-\frac{1}{\tau} (1 - n_{e, F}^r) t} \left\{ \langle S_Q(k) \rangle_F^{(0)} + \frac{\alpha_{e, F}}{\tau} \sum_{n_{e, F}^r \neq n_{e, F}^r} \int_0^t dt' e^{(i(\omega_{e, q} - \omega_{e, q}) + \frac{1}{\tau} (1 - n_{e, F}^r) t')} \right\} + \sum_{n_{e, F}^r \neq n_{e, F}^r} e^{-\frac{1}{\tau} (1 - n_{e, F}^r) t} \left\{ \left( \langle S_Q(k) \rangle_F^{(0)} \right) + \frac{\alpha_{e, F}}{\tau} \sum_{n_{e, F}^r \neq n_{e, F}^r} \int_0^t dt'' \langle S_Q(k) \rangle_F^{(1)} \right\}
\]

or

\[
\langle S_Q(k) \rangle_F' = e^{-\frac{1}{\tau} (1 - n_{e, F}^r) t} \left\{ \langle S_Q(k) \rangle_F^{(0)} + \frac{\alpha_{e, F}}{\tau} \sum_{n_{e, F}^r \neq n_{e, F}^r} \int_0^t dt'' \langle S_Q(k) \rangle_F^{(1)} \right\} + \mathcal{O} \left( \frac{1}{\tau} \right)
\]

(3.96)

Since \( \frac{1}{\tau} \ll \omega \), one can now employ the secular approximation in (3.97) by assuming terms on the order of \( \frac{1}{\tau} \omega \) are negligible. This means that the sum over \( n_{e, F}^r \) and all succeeding terms in the iteration can be ignored. The time dependence of \( \langle S_Q(k) \rangle_F' \) is then

\[
\langle S_Q(k) \rangle_F' = e^{-\frac{1}{\tau} (1 - n_{e, F}^r) t} \left\{ \langle S_Q(k) \rangle_F^{(0)} + \frac{\alpha_{e, F}}{\tau} \sum_{n_{e, F}^r \neq n_{e, F}^r} \int_0^t dt'' \langle S_Q(k) \rangle_F^{(1)} \right\}
\]

(3.98)

So that by using (3.98) in (3.90) one finds for \( Q \neq 0 \)

\[
\langle S_Q(k) \rangle_F = e^{-\frac{1}{\tau} (1 - n_{e, F}^r) t} \langle S_Q(k) \rangle_F^{(0)} + \frac{\alpha_{e, F}}{\tau} \sum_{n_{e, F}^r \neq n_{e, F}^r} \int_0^t dt'' \langle S_Q(k) \rangle_F^{(1)}
\]

(3.99)
Since the values for \(< S_q(k) >_F\) are now known, all the possible \(< T_q(k) >_F\)'s are known. To see this, consider equation (3.64). Use the Wigner-Eckart theorem (A.5) to write

\[
<T_q(k)>_F = \sum_{mm'} <F \| T(k) \| F'> (-)^{F-m'} \frac{<F \| S_q(k) \| F'>}{<F \| S(k) \| F'} (3.100)
\]

Again by the Wigner-Eckart theorem, the 3-J symbol can be replaced with

\[
(-)^{F-m'} \frac{<F \| S_q(k) \| F'>}{<F \| S(k) \| F'} (3.101)
\]

so that (3.100) can be written

\[
<T_q(k)>_F = \frac{<F \| T(k) \| F'>}{<F \| S(k) \| F'} \sum_{mm'} <F \| \rho \| F'> <F \| S_q(k) \| F'> (3.102)
\]

For the \(Q=0\) terms the solution for \(< T_0(k) >\) is particularly easy. Sum (3.102) over \(F\). Since \(\mathcal{C}\) and \(\tau_{\mathcal{K}}\) are independent of \(F\), \(< T_0(k) >\) will be a sum of two decays as is (3.88); only the weighting factors will differ.

\[
<T_0(k)> = e^{-t/\mathcal{C}} \left[ \sum_F \frac{<F \| T(k) \| F'>}{<F \| S(k) \| F'>} \left( <S_0(k)>_F - \frac{\alpha_{F,K}}{\sum_{F'} \alpha_{F',K}} <S_0(k)>_F \right) \right] +
\]

\[
e^{-t/\tau_{\mathcal{K}}} \left[ \sum_F \frac{<F \| T(k) \| F'>}{<F \| S(k) \| F'>} \cdot \frac{\alpha_{F,K}}{\sum_{F'} \alpha_{F',K}} <S_0(k)>_F \right] (3.103)
\]
A similar procedure is to be followed for $Q \neq 0$ terms. The answer, however, is much more complicated as there is one time constant for each $F$. Typical observables of interest for $\langle T_0(k) \rangle$ would be the nuclear polarization $\langle \bar{I} \rangle$ and the total atomic polarization $\langle \bar{P} \rangle$.

\section{Time Dependence of $\rho$}

Since the $\langle T_0(k) \rangle$ are known for all $K$ and $Q$, the density matrix is also known. Recall equations (3.6) and (3.7) which together imply

$$\rho_{i}(\xi) = \sum_{K} \langle T_{KQ}(FF) \rangle T_{KQ}(FF)$$

(3.104)

Hence, since all $\langle T_{KQ}(FF) \rangle$'s are known from equation (3.77) for $K=0$ and equation (3.102) for $K \neq 0$, in conjunction with either equation (3.38) for $Q=0$ or equation (3.92) for $Q \neq 0$, the atomic density matrix is completely specified for the given assumptions.

This method of finding time constants is quite straightforward and assumes only the same physical assumptions that Gross et al.\textsuperscript{20} assumed. However, it is much more general. The only additional assumptions made were that electron spin not enter into the charge exchange collision and that both nuclear and electronic spin be half integral. With these assumptions, one can find the time dependence of the expectation value of any angular momentum tensor operator.
A specific example is given in Chapter V.
CHAPTER IV

INCLUSION OF ADDITIONAL RELAXATION MECHANISMS
FOR THE ATOMIC SYSTEM

In the previous chapter the evolution of the density matrix for the atomic system due to charge exchange collisions was derived. However, not only are the atoms interacting with the ions by means of charge exchange collisions, but they are also affected by collisions with the walls and the buffer gas atoms and they interact with the pumping light. All these contributions must be included in some fashion into a master equation for the time evolution of the density matrix for the atomic system. Symbolically the atomic master equation becomes

$$\frac{d}{dt} \rho = -i \{ H, \rho \} + \frac{\partial}{\partial t} \left( \rho_{ee} \right) + \frac{\partial}{\partial t} \left( \rho_{coll} \right) + \frac{\partial}{\partial t} \left( \rho_{pump} \right)$$

where $H$ is as before

$$H = \hat{A} \hat{B} \cdot \hat{S} - \mu \gamma \frac{H_o F_2}{2}$$

and, as derived in the last chapter, $\frac{\partial}{\partial t} \left( \rho_{ee} \right)$ is given by

$$\frac{\partial}{\partial t} \left( \rho_{ee} \right) = -\frac{1}{\tau} \left[ \rho_{ee} - \rho_{ee}^{eq} \right]$$

with $\tau$ given by equation (3.14).
1. Collisional Relaxation Mechanisms

Since random spin disorienting collisions, such as those with the wall or the buffer gas tend to drive the system to thermal equilibrium, the spin relaxation will be handled phenomenologically by assuming an exponential decay of the atomic polarization resulting in Bloch type equations. The matrix elements of $\frac{d\hat{\rho}}{dt}$ due to random collisions are therefore

$$\frac{d}{dt} \langle FM | \rho | IFM' \rangle_{\text{collision}} = -\frac{i}{T_i} \left[ \langle FM | \rho | IFM' \rangle - \frac{1}{(2S+1)(2I, +1)} \right] \quad (4.2)$$

and

$$\frac{d}{dt} \langle FM | \rho | IFM' \rangle_{\text{collision}} = -\frac{i}{T_L} \langle FM | \rho | IFM' \rangle \quad (4.3)$$

The diagonal density matrix elements all relax exponentially to $\frac{1}{(2S+1)(2I, +1)}^{-1}$ with the longitudinal relaxation time $T_L$, where the small population differences between eigenstates of $F_z$ due to the Boltzmann distribution at thermal equilibrium have been ignored. Note that the constant in equation (4.2) was chosen such that $Tr \rho_i = 1$ as before. Since in thermal equilibrium there is no coherent precession of the spins about the z axis, the off diagonal density matrix elements relax to zero with the transverse relaxation time $T_2$. To see that the Bloch equations
result from equations (4.2) and (4.3), consider the time
development of $\langle F_z \rangle$ and $\langle F_\pm \rangle$ due to collisional relaxation
alone. Since

$$\langle \vec{F} \rangle = T \rho \vec{F} \quad (4.4)$$

and therefore

$$\frac{d}{dt} \langle \vec{F} \rangle = T \rho \frac{d\rho}{dt} \vec{F} \quad (4.5)$$

one can write

$$\frac{d}{dt} \langle F_z \rangle = -\frac{1}{T_z} \langle F_z \rangle \quad (4.6a)$$

and

$$\frac{d}{dt} \langle F_\pm \rangle = -\frac{1}{T_\pm} \langle F_\pm \rangle \quad (4.6b)$$

Specifically for the case of diffusion to uncoated walls in
the presence of a buffer gas at low pressure, Massnou-Seeuws
and Bouchiat\textsuperscript{10} have found that the spin relaxations is of the
form

$$\frac{d}{dt} \langle F_z \rangle = -\frac{1}{T_{\text{can}}} \langle J_z \rangle - \frac{1}{T_{\text{wall}}} \langle F_z \rangle \quad (4.7)$$

However, as pointed out by Balling\textsuperscript{24} when the buffer gas
pressure is low enough the wall collisions will dominate
and the form of the spin relaxation will be as assumed in equations (4.6)

2. Effect of the Pumping Light

The main effect of the pumping light is to redistribute the ground state populations. As a result there is a ground state lifetime due to the pumping that depends on the intensity of the incoming light and the lifetime of the excited state. The light also tends to cause a slight shift in the ground state energy levels due to virtual absorption. A detailed theory of the interaction of the light with an atom having no hyperfine structure using second order time dependent perturbation theory can be found in Cohen-Tannoudji's thesis and in the articles by Barrat and Cohen-Tannoudji. A summary of this work can be found in Les Houches. Balling has performed a similar calculation including the effect of the hyperfine structure. Using first order time dependent perturbation theory he derived the effect of the light for the case of D1 absorption from an \( \text{S}_{\frac{1}{2}} \) ground state, assuming complete re-orientation of the excited state, constant pumping light intensity throughout the cell, and \( \Delta M = \pm 1 \) absorption. The results are the following:

for the diagonal elements

\[
\frac{\partial}{\partial t} \langle \mathcal{F} M | \rho | \mathcal{F} M \rangle_{\text{light}} = -\frac{1}{T_p} \left( I + \frac{2M}{2I+1} \right) \langle \mathcal{F} M | \rho | \mathcal{F} M \rangle +
\]

\[
\frac{1}{(2S+1)(2I+1)} \sum_{\mathcal{P} \mathcal{H} \mathcal{H}'} \frac{1}{T_p} \left( I + \frac{2M'}{2I' + 1} \right) \langle \mathcal{F} M' | \rho | \mathcal{F} M' \rangle
\]

\[(4.8)\]
and for the off-diagonal elements

\[ \frac{\partial}{\partial t} \langle \mathcal{E}_{M} \rho_{1} \mathcal{E}_{M'} \rangle_{\text{light}} = -\frac{i}{T_{p}} \left[ | \mathcal{E}_{M} \mathcal{E}_{M'} \rangle \langle \mathcal{E}_{M} \mathcal{E}_{M'} | + \right. \\
\left. i \Delta E_{m,m'} \langle \mathcal{E}_{M} \rho_{1} \mathcal{E}_{M'} \rangle \right. \tag{4.9} \]

The first term on the right hand side of equation (4.8) is the result of the first order calculation for the effect of the pumping light on a ground state sublevel. The second term is due to the complete reorientation of the excited state sublevels due to collisional mixing. The actual population distribution due to excited state mixing is discussed by Franz and Franz, however, for ease in calculation, complete mixing is assumed here. The right hand side of equation (4.9) shows the evolution of the Zeeman coherence in the ground state due to the pumping plus a term describing the shift due to virtual absorption. The cross term between different hyperfine levels has been ignored because it is being assumed that

\[ \langle \mathcal{E}_{M} \rho_{1} \mathcal{E}_{M'} \rangle = \delta_{F,F'} \langle \mathcal{E}_{M} \rho_{1} \mathcal{E}_{M'} \rangle \]

In equations (4.8) and (4.9) the following notation has been used

\[ F = I, \pm \frac{1}{2} \tag{4.10} \]

and

\[ \frac{1}{T_{p}} = 4 \pi^{2} \alpha \omega_{0} \langle \frac{1}{2} \parallel D \parallel \frac{1}{2} \rangle^{2} \int_{0}^{\infty} I(\omega) e^{-\frac{M^{2}}{2kT} \frac{(\omega_{0} - \omega)^{2}}{\omega_{0}^{2}}} d\omega \]

\[ \int_{0}^{\infty} e^{-\frac{M^{2}}{2kT} \frac{(\omega_{0} - \omega)^{2}}{\omega_{0}^{2}}} d\omega \]
where \( \alpha \) is the fine structure constant, \( \omega \), the frequency of the light before being Doppler shifted, and \( \mathcal{D} \) is proportional to the dipole moment of the atom. It has been tacitly assumed that the two hyperfine components in the pumping radiation are equal in intensity.

### 3. Combined Effect

At this point one can include all of the effects into an atomic master equation. The equation for the diagonal elements is written

\[
\frac{d}{dt} \langle FM_1 \rho_1 FM \rangle = -\frac{i}{\hbar} \left[ \langle FM_1 \rho_1 FM \rangle - \frac{1}{2} \sum_{F''} \frac{\mathcal{D}^{F''}_{F''}}{2F'' + 1} \langle 2F'' + 1 \rangle - \frac{1}{T_t} \left[ \langle FM_1 \rho_1 FM \rangle - \frac{1}{2(2F'' + 1)} \right] - \frac{1}{T_p} \left[ \langle FM_1 \rho_1 FM \rangle - \frac{1}{2(2F'' + 1)} \right] \right]
\]

\[
+ \frac{1}{2(2F'' + 1)} \sum_{F'M'} \frac{1}{T_p} \left[ \langle FM_1 \rho_1 FM \rangle - \frac{1}{2F'M'} \right] \langle F'M' \rho_1 F'M' \rangle
\]

while for the off-diagonal elements the master equation becomes

\[
\frac{d}{dt} \langle FM_1 \rho_1 FM' \rangle = i \mu_0 g_F H_0 (M' - M) \langle FM_1 \rho_1 FM' \rangle - \frac{1}{\hbar} \left[ \langle FM_1 \rho_1 FM' \rangle - \frac{1}{2} \sum_{F''} \frac{\mathcal{D}^{F''}_{F''}}{2F'' + 1} \langle 2F'' + 1 \rangle - \frac{1}{T_t} \left[ \langle FM_1 \rho_1 FM' \rangle - \frac{1}{2(2F'' + 1)} \right] - \frac{1}{T_p} \left[ \langle FM_1 \rho_1 FM' \rangle - \frac{1}{2(2F'' + 1)} \right] \right] \]

\[
+ \frac{1}{2(2F'' + 1)} \sum_{F'M'} \frac{1}{T_p} \left[ \langle FM_1 \rho_1 FM' \rangle - \frac{1}{2F'M'} \right] \langle F'M' \rho_1 F'M' \rangle
\]
Inspection of equations (4.12) and (4.13) will reveal that they are uncoupled; the evolution of a diagonal element depends only on other diagonal elements while the evolution of an off-diagonal element depends solely on other off-diagonal elements.

Now that the full equation has been developed, consider its solution for two observables of interest, the hyperfine level populations and the atomic polarization.

For the hyperfine populations

\[ \sigma_F = \sum \langle F_M | \rho, 1F M' \rangle \]  

(4.14)

one finds

\[ \frac{d}{dt} \sigma_F = - \left( \frac{1}{\tau} + \frac{1}{\tau_I} + \frac{1}{\tau_p} \right) \left( \sigma_F - \frac{2F+1}{(2S+1)(2I,+1)} \right) \]  

(4.15)

\[ \pm \frac{2}{\tau_p (2I,+1)} \left[ \langle F_\sigma \rangle_F - \frac{2F+1}{(2S+1)(2I,+1)} \langle F_\sigma \rangle \right] \]
Similarly for the atomic polarization, defined to be

$$\langle F_z \rangle_F = \sum_M \langle FM | \rho_1 | FM \rangle$$  \hspace{1cm} (4.16)

one finds that every term except the exchange term is straightforward. To evaluate the exchange term, reexpress $$\langle FM | F_z | FM \rangle$$ in terms of its reduced matrix element and a 3-J symbol by using the Wigner-Eckart theorem, equation (A.5). Then using (A.16) one finds

$$\frac{d}{dt} \langle F_z \rangle_F = - \left( \frac{1}{t} + \frac{1}{T_1} + \frac{1}{T_p} \right) \langle F_z \rangle_F \pm \frac{2}{T_p} \langle F_z^2 \rangle_F +$$

$$\pm \frac{1}{T} \sum_{F''} (-1)^{F''} \left( \frac{2F+1}{2F''+1} \right) \left( \frac{2F(F+1)(2F''+1)}{(2I, + 1)} \right) \left( \frac{2F''(F''+1)}{(2I', + 1)} \right) \left\{ \begin{array}{c} S \ F \ I, \ F'' \ I' \\ F' \ S' \ F'' \end{array} \right\} \langle F_z F'' \rangle_F$$  \hspace{1cm} (4.17)

Equations (4.15) and (4.17) are very difficult to solve because they contain higher powers of $F_z$ in the right hand side than on the left hand side. This is due to the $m$ dependence in the pumping terms

$$\frac{1}{T_p} \left( \frac{M}{2I_{1/2}} \right) \quad \text{or} \quad \frac{1}{T_p} \left( \frac{M+M'}{2I_{1/2}} \right)$$  \hspace{1cm} (4.18)

in equations (4.12) and (4.13). In order to estimate the effect of the pumping, circumvent this problem in the same way as Balling by replacing the expression (4.18) by and "average" pumping time $1/T_p'$. Equations (4.12) and
(4.13) then become

$$\frac{d}{dt} \langle FM | \rho, 1FM \rangle = -\frac{i}{\hbar} \left[ \langle FM | \rho, 1FM \rangle - \sum_{F'''m'''} (-)^{F''m'''} \langle F''m'' | \rho, 1F''m'' \rangle \right]$$

$$\times \frac{(2F+1)}{(2I+1)} \times \frac{(2F'+1)}{(2I'+1)}$$

(4.19)

$$- \left( \frac{1}{T_I} + \frac{1}{T_p'} \right) \left[ \langle FM | \rho, 1FM \rangle - \frac{1}{(2F+1)(2I+1)} \right]$$

and

$$\frac{d}{dt} \langle FM | \rho, 1FM' \rangle = i \mu_0 g_0 H_0 (M-M') \langle FM | \rho, 1FM' \rangle -$$

$$-\frac{i}{\hbar} \left[ \langle FM | \rho, 1FM' \rangle - \sum_{F''m''} (-)^{F''m''} \langle F''m'' | \rho, 1F''m'' \rangle \right]$$

$$\times \frac{(2F+1)}{(2I+1)} \times \frac{(2F'+1)}{(2I'+1)}$$

(4.20)

$$- \left( \frac{1}{T_I} + \frac{1}{T_p'} \right) \langle FM | \rho, 1FM' \rangle$$

where the energy shift term has been ignored in (4.20).

Note that by using an effective pumping time $T_p'$ the equa-
tions are again uncoupled. As one can see from inspection of equations (4.19) and (4.20) the effects of the additional relaxation mechanisms is to change the time constants. For example, first consider the development of the hyperfine populations under the combined influences of charge exchange collisions, collisional relaxation, and the pumping light. By summing (4.19) over \( m \) one finds

\[
\frac{d}{dt} \sigma_F = -\left( \frac{1}{\tau} + \frac{1}{T_1} + \frac{1}{T_\rho'} \right) \left( \sigma_F - \frac{2F_+}{(2F+1)(2I+1)} \right) \tag{4.21}
\]

Again one finds a single time constant decay, however, the new time constant is different from the one previously found; it is smaller by the factor

\[
\frac{1}{1 + \frac{1}{\tau} \left( \frac{1}{T_1} + \frac{1}{T_\rho'} \right)} \tag{4.22}
\]

Now consider the observable \( \langle S_q(\kappa) \rangle_F \). Recall that under the sole effect of charge exchange collisions, it decayed with only one time constant \( \tau'_\kappa \), equation (3.84). Now, however, the time constant is

\[
\frac{1}{\tau'_\kappa} = \frac{1}{\tau} \left( 1 - \frac{2F_+}{(2F+1)} \right) \left( \frac{S F I_1}{I_1} \right)^{\frac{1}{2}} + \frac{1}{T_1} + \frac{1}{T_\rho'} \tag{4.23}
\]

The equations that follow equation (3.83) are then still valid in form but the following substitutions must be made for the two time constants \( \tau \) and \( \tau'_{\kappa} \).
Similarly for $Q_d \sigma$ equation (3.99) becomes, using equation (4.20)

\[
\frac{1}{\tau} \rightarrow \frac{1}{\tau'} = \frac{1}{\tau} + \frac{1}{\tau_i} + \frac{1}{\tau_p},
\]

\[
\frac{1}{\tau''_K} \rightarrow \frac{1}{\tau''_K} = \frac{1}{\tau'_{K}} + \frac{1}{\tau_i} + \frac{1}{\tau_p},
\]  \hspace{1cm} (4.24)

Addition of the other relaxation mechanisms was found to shorten the decay time constants for the $\langle T_q(\kappa) \rangle's$, thereby altering the time dependence of the density matrix numerically but not in form. In order to study the effect of the charge exchange collisions care must be taken to keep the pumping light as weak as possible and therefore $1/\tau_p$ as small as possible while still allowing the experiment to be performed. This will also make the effect of the assumption of an effective pumping time negligible as the pumping light will then have only a small effect on the density matrix. The size of the collisional relaxation term tends to be small for the usual experimental conditions.
CHAPTER V

ANALYSIS OF A NUCLEAR SPIN 3/2 SYSTEM

In the previous chapters general formulas were developed to find the time dependence of the multipole polarizations of an alkali atom under the following assumptions: (1) the polarization of the alkali ion be maintained at zero by means of a resonant r-f field, (2) the secular approximation is valid, and (3) there is no hyperfine coherence in the ground state. With these general formulas one can predict the time development of any specific angular momentum operator in the system. In this chapter a specific example will be discussed and some of the formulas numerically evaluated.

Take, for example Rb$^{87}$. This isotope has a nuclear spin of 3/2. The $S_{1/2}$ ground state and $P_{1/2}$ excited states therefore each have two $F$ levels, $F=1$ and $F=2$, as was shown in figure 5. First consider the time development of a hyperfine population $P_F$.

Under the influence of charge exchange collisions alone its time development is that of a single exponential as can be seen in equation (3.77). Assuming Mitchell and Fortson's $^{42,43}$ experimental setup as given in Chapter I, one can find the time constant to be
\[
\frac{1}{\tau} = N_{\text{Rb}} \sigma_{Ce} \langle \nu \rangle_{\text{Rb-Rb}^+} = 2.9/3.
\]

or

\[
\tau = 34.4 \text{ ms.} \tag{5.1}
\]

where the charge exchange cross section was assumed to be

\[
\sigma_{Ce} = 7.1 \times 10^{-19} \text{ cm}^2
\]

and the Rb ion density \(10^{10}\) ions/cc.

The average value of the velocity was found from kinetic theory. \(51\)

\[
\langle \nu \rangle_{\text{Rb-Rb}^+} = \sqrt{\frac{8 kT}{\pi}} \left( \frac{1}{M_{\text{Rb}}} + \frac{1}{M_{\text{Rb}^+}} \right) = 4.1 \times 10^4 \text{ cm. /sec.}
\]

Note that as expected this frequency is much smaller than either the hyperfine frequency (\(\sim 6.8 \times 10^9\) Hz.)\(^{24}\) or the Zeeman frequency (\(\sim 7.0 \times 10^6\) Hz.). Thus the secular approximation is obviously valid in this case. When other effects are included, the charge exchange frequency is increased slightly, but not so that it is at all comparable with the Zeeman frequency. If one assumes that the leading correction to \(\tau\) is that due to wall collisions, the new time constant is found to be\(^9\)

\[
\frac{1}{\tau'} = \frac{1}{\tau} + \frac{1}{\tau_{\text{wall}}} = 30.1/3.
\]

or

\[
\tau' = 33.2 \text{ ms.} \tag{5.2}
\]
The effect is approximately a 3% decrease in the time constant.

The approximation that \( \tau_{\text{gas}} \gg \tau_{\text{wall}} \) is valid here since

\[ \tau = 70^\circ \text{C}, \quad p_{\text{He}} = 30 \text{ Torr} \]  \[ \text{43} \]

With these numbers and \( \sigma_{\text{Rb-He}} \) taken from Bernheim, one finds

\[
\frac{1}{\tau_{\text{gas}}} = N_{\text{He}} \sigma_{\text{Rb-He}} \langle \nu' \rangle_{\text{Rb-He}}
\]

\[
= \left( 1.06 \times 10^{18} \ \text{atoms} \right) \left( 6.2 \times 10^{-25} \ \text{cm}^2 \right) \left( 1.4 \times 10^5 \ \text{cm} / \text{sec} \right)
\]

\[
\approx 9.2 \times 10^{-2} \ \text{Hz}
\]

So

\[
\tau_{\text{gas}} \approx 10.9 \text{ sec}.
\]  \[ (5.3) \]

which is an order of magnitude larger than \( \tau_{\text{wall}} \). The pumping time is assumed to be kept large by keeping the intensity of the incoming light low.

As an example of the effects of the charge exchange collisions on the density matrix elements, assume that initially the atoms were oriented by means of \( \sigma^+ \) light and therefore are in the stretched state

\[
|FM\rangle_{\text{initial}} = 1^2 2^> \]  \[ (5.4) \]

The initial density matrix is then

\[
\langle FM | \rho_{\text{initial}} | FM' \rangle = \delta_{F_1} \delta_{F_1'} \delta_{M_2} \delta_{M_2'}
\]  \[ (5.5) \]

Since the effects of other mechanisms have been shown to be small, ignore them here and use the formulas developed in
chapter III. All times will be given in milliseconds.

With the above assumptions, the two hyperfine populations evolve using equation (3.77) as

\[ \sigma_1 = \frac{3}{8} \left( 1 - e^{-t/3\gamma_4} \right) \]

\[ \sigma_2 = \frac{1}{8} \left( 5 + 3 e^{-t/3\gamma_4} \right) \]

As expected the population of the lower hyperfine level increases in time so that \( \sigma^+ \) light may again be absorbed from the incoming beam.

Next consider the evolution of \( \langle S_z \rangle \), \( \langle F_z \rangle \), and \( \langle T_z \rangle \). Since according to equation (3.102) \( \langle F_z \rangle \) and \( \langle T_z \rangle \) depend on \( \langle S_z \rangle \), one must know \( \langle S_z \rangle \). From equation (3.64)

\[ \langle S_z \rangle = \sum_{m,m'} \langle FM|M_{F}\rangle \langle FM'|S_z|FM'\rangle \]

But from equation (5.5) this becomes

\[ \langle S_z \rangle = \langle 2 2 1 S_z 1 2 2 \rangle \delta_{F,2} \]

Use of the Wigner-Eckart theorem (A.5) gives

\[ \langle S_z \rangle = \left( \begin{array}{cc} 2 & 1 \\ -2 & 0 \end{array} \right) \langle 2 || S || 2 \rangle \delta_{F,2} \]

The 3-J symbol can be found in Edmonds and the reduced
matrix element can be found from equations (A.29) and (A.26) to be $\sqrt{\frac{e}{8}}$. As a result one finds

$$\langle S_\mathcal{2} \rangle_{t=0} = \frac{1}{2} \delta_{\mathcal{F}, 2} \tag{5.10}$$

By summing equation (5.10) over $\mathcal{F}$ one immediately finds

$$\langle S_\mathcal{2} \rangle_{t=0} = \frac{1}{2} \tag{5.11}$$

as expected since the initial state is the stretched state. In order to find the evolution of $\langle S_\mathcal{2} \rangle$ one needs to know $\gamma'$. Recall equation (3.84)

$$\frac{1}{\tau'_k} = \frac{1}{\tau} \left[ 1 - \sum_{\mathcal{F}} \frac{(2 \mathcal{F} + 1)}{(2 \mathcal{I} + 1)} \left\{ S_{\mathcal{F}, \mathcal{I}} \right\}^k \right] \tag{5.12}$$

Specifically for Rb$^87$ and $k = 1$, (5.12) gives

$$\frac{1}{\tau'_1} = \frac{1}{\tau} \left[ 1 - 2 \frac{(2 \mathcal{F} + 1)}{(2 \mathcal{I} + 1)} \left\{ S_{\mathcal{F}, \mathcal{I}} \right\}^1 \right] = \frac{\delta}{8} \cdot \frac{1}{\tau}$$

so

$$\tau'_1 = \frac{\delta}{5} \quad \tau = 55 \text{ ms.} \tag{5.13}$$

Using equations (3.83), (5.11), and (5.13), one finds for $\langle S_\mathcal{2} \rangle$

$$\langle S_\mathcal{2} \rangle = \frac{1}{2} e^{-\frac{t}{55}} \tag{5.14}$$

Equation (3.88) and the above information also give the time
evolution of the $<s_z>_p$'s which are needed to find $<F_z>$ and $<I_z>$. 

\[
<s_z>_1 = -\frac{1}{\gamma} \left[ e^{-t/3\gamma} - e^{-t/5\gamma} \right] \quad (5.15a)
\]

and

\[
<s_z>_2 = \frac{1}{\gamma} \left[ e^{-t/3\gamma} + 5 e^{-t/5\gamma} \right] \quad (5.15b)
\]

The combination of equations (5.15) with (3.102) and (A.26) for the reduced matrix elements gives

\[
<F_z>_1 = -4 <s_z>_1 \quad (5.16a)
\]

and

\[
<F_z>_2 = 4 <s_z>_2 \quad (5.16b)
\]

or combining the above

\[
<F_z> = 4 \left[ <s_z>_2 - <s_z>_1 \right]
\]

\[
= \frac{2}{3} \left[ e^{-t/3\gamma} + 2 e^{-t/5\gamma} \right] \quad (5.17)
\]

Again the disorienting effect of the charge exchange collisions can be seen. Initially $<F_z> = 2$. Due to the charge exchange collisions, it then decays to zero with two time constants. This is the same effect that occurs in spin
exchange collisions\textsuperscript{20}.

Finally consider the evolution of $\langle I_z \rangle$. Using equations (A.30) and (A.26) for the reduced matrix elements, one finds

$$\langle I_z \rangle = -5 \langle S_z \rangle,$$

(5.18a)

and

$$\langle I_z \rangle = 3 \langle S_z \rangle$$

(5.18b)

If the above two equations are added together, one finds that their sum is just $\langle F_z \rangle - \langle S_z \rangle$ as it should be.

In summary the three polarizations are

$$\langle S_z \rangle = \frac{1}{2} e^{-t/55},$$

$$\langle F_z \rangle = \frac{2}{3} \left[ e^{-t/34.4} + 2 e^{-t/55} \right]$$

$$\langle I_z \rangle = \frac{1}{6} \left[ 4 e^{-t/34.4} + 5 e^{-t/55} \right]$$

The example of Rb\textsuperscript{87} initially in the stretched ground state clearly shows the expected one and two time constant decays for the various polarizations. One can also see the single decay time for the hyperfine populations. Note that its time decay is different from the one for $\langle S_z \rangle$. The time decay of higher order operators can also be found by using the same method as was used here for the first order tensor operators.
CHAPTER VI

CONCLUSION

The scattering matrix for resonant charge exchange collisions between ions and their parent nuclei was found assuming slow collisions and taking into account the identity of the nuclei. The equations governing the charge exchange process were seen to be very similar to those governing electron spin exchange collisions except for the complications arising from identical nuclei and higher order spin. Comparison with charge exchange cross sections for zero nuclear spin showed that the scattering matrix derived here is a generalization of the known form for the zero nuclear spin charge exchange scattering cross section.

Once the scattering matrix was known, the effect of the charge exchange collisions on various multipole polarizations and therefore the atomic density matrix was found assuming the secular approximation, no hyperfine coherence in the ground state, and \( \langle T_{KQ} (I_z, I_z) \rangle \propto \delta_{k_0} \delta_{Q0} \). The general form for the time development of the polarizations was seen to be quite simple and a great deal of latitude was given for the choice of angular momentum observable. The characteristic two time constant decay was found for \( \langle F_z \rangle \) and \( \langle I_z \rangle \). \( \langle S_z \rangle \) and \( \sigma_z \), however, decayed with only single time constants. As was seen in Chapter V, numerical results involved simple evaluation of
angular momentum coupling coefficients. In Chapter IV the effects of other relaxation mechanisms were considered and seen to have only a small effect for the chosen experimental conditions.

The scattering matrix found in Chapter II was used here for the specific problem of finding the time dependence of the atomic density matrix, assuming the initial conditions are known. A further possible calculation would be to find the effect of a strong constant magnetic field instead of a weak field. One could also calculate the line shape and frequency shift for the equilibrium signal as was done in BHF\textsuperscript{14} for spin exchange collisions. The formalism used here could be used to analyze further the decay of the density matrix due to spin exchange collisions. Finally, it is hoped that this analysis would allow for quantitative determination of charge exchange cross sections at low energies.
BIBLIOGRAPHY


APPENDIX A

SPHERICAL TENSOR OPERATORS

In this appendix many relationships for spherical tensor operators are given with indications of their derivations. Spherical tensor operators are defined to be those tensors which transform under rotation as the spherical harmonics do. For a rotation of $\Theta$ of the frame of reference about the direction $\hat{n}$, the following relationship from Edmonds$^{52}$ is true for these operators:

$$R T_q(k) R^{-1} = \sum_{Q'} T_{Q'}(k) D_{Q'Q}^K(R)$$  \hspace{1cm} (A.1)

with $R = e^{i \Theta \hat{n} \cdot \vec{J}}$ and $D_{Q'Q}^K(R) = \langle KQ' | R | KQ \rangle$

$T_q(k)$ is any tensor operator of rank $K$ and component $Q$.

By assuming a small angle of rotation, one can derive the commutation relations of the tensor operators with total angular momentum $\vec{J}$:

$$[\vec{J} \cdot \hat{n}, T_q(k)] = \sum_{Q'} T_{Q'}(k) \langle KQ' | \vec{J} \cdot \hat{n} | KQ \rangle$$

or specifically

$$[J_z, T_q(k)] = Q T_q(k)$$  \hspace{1cm} (A.2)

$$[J_{\pm}, T_q(k)] = i[K(K+1) - Q(Q \pm 1)] T_{Q\pm1}(k)$$

Since the tensor operators can be expressed as a linear combination of outer products of angular momentum eigenvectors $|J M\rangle$ (the standard expansion of operators
which are angular momentum dependent), one can choose either the \( |JM \rangle \langle J'M'| \) or a normalized set of spherical tensor operators as a basis for expanding an arbitrary operator. For example, consider the operator \( \mathcal{A} \). One would normally write

\[
\mathcal{A} = \sum_{JM} |JM \rangle \langle J'M'| <JM|A|J'M>|
\]

The operator \( \mathcal{A} \) can also be expressed in terms of the normalized spherical tensor operators \( T_{Kq}(JJ') \) as

\[
\mathcal{A} = \sum_{JJ'} T_{Kq}(JJ') \mathcal{A}_{KQ}(JJ')
\]

where prematurely using equation (A.8) it can be seen that

\[
\mathcal{A}_{KQ}(JJ') = T_{Kq} \mathcal{A} T_{Kq}^+ (JJ') = \sum_{J'M'} <J'M'|A|J'M>| T_{Kq}^+ (JJ') |J'M'>
\]

which from (A.9) and (A.11) is seen to be

\[
\mathcal{A}_{KQ}(JJ') = \sum_{mm'} (-)^{J-m} \left( \begin{array}{c} J \ K \ J' \\ m \ Q \ m' \end{array} \right) \sqrt{2K+1} <JM|A|JM'>
\]

Note that, as in Chapter III, \( T_{Kq}(JJ') \) is a basis spherical tensor operator while \( \mathcal{T}_Q(k) \) is an arbitrary spherical tensor operator of rank \( k \) and component \( Q \). In each case \( \mathcal{A} \) was expressed in terms of a sum of basis operators weighted by an expansion coefficient. One advantage of using the \( T_{Kq} \) basis instead of \( |JM \rangle \langle J'M'| \) is that the \( T_{Kq} \) formalism naturally yields the multipole moments of the operators, thereby making the application of physical assumptions to the problem at hand more
transparent analytically. This is the reason they are used here.

Following is a list of formulas for the spherical tensor operators. They can all be proved using basic relationships and standard references, such as Edmonds and Brink and Satchler. It is useful to note that 
\((-1)^{t+\frac{3}{2}} = (-1)^{t-\frac{3}{2}}\), but 
\((-1)^{t} \neq (-1)^{t+\frac{3}{2}}\). For this reason, powers of \(-1\) that add to an integer are bracketed. Two such square brackets can be added or subtracted as desired but the relative signs of terms within a bracket may not be altered.

To find the linking equation between the two bases, express \(T_K \Phi^{(2)}\) in terms of \(IJM\) \(\langle j' m' \rangle\):

\[
\bar{T}_{KQ} (jj') = \sum_{m m'} \langle j m | j' m' \rangle \langle j m | T_{KQ} \langle j' m' \rangle
\]

Due to the transformation properties of the \(T_{KQ}\) 's, the geometrical (\(Q\) dependence) and physical (\(K\) dependence) of their matrix elements can be computed independently of each other and then multiplied together. This is known as the Wigner-Eckart theorem:

\[
\langle j m | T_{Q}(k) | j' m' \rangle = (-)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix} \langle j m | T(k) | j' m' \rangle
\]

\[
(A.5)
\]

Then

\[
\bar{T}_{KQ} (jj') = \sum_{m m'} \langle j m | j' m' \rangle (-)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix} \langle j m | T(k) | j' m' \rangle
\]
The reduced matrix element $\langle \mathcal{J} \parallel T(K) \parallel \mathcal{J}' \rangle$ is a normalization constant in this case which can be freely chosen. This is usually accomplished by assuming that the $T_{kq}$'s obey some sort of orthogonality relationship:

$$
T_{2} T_{kq} (J_{1}, J_{2}) T_{K}^{+}, (J_{3}, J_{4}) = \sum_{\mathcal{J}} \langle \mathcal{J} \parallel T_{kq} (J_{1}, J_{2}) T_{K}^{+}, (J_{3}, J_{4}) \parallel \mathcal{J} \rangle \mathcal{J} \mathcal{J}
$$

$$
= \delta_{J_{1}, J_{3}} \delta_{J_{2}, J_{4}} \delta_{K, K'} \delta_{Q, Q'} \frac{1}{2 \; K + 1} | \langle \mathcal{J} \parallel T(K) \parallel \mathcal{J}' \rangle |^{2}
$$

where Edmonds (3.7.8) was used:

$$
\sum_{J_{3} J_{4} J_{5}} (2 J_{3} + 1) \begin{pmatrix} J_{1}, J_{2}, J_{3} \end{pmatrix} \begin{pmatrix} J_{1}, J_{2}, J_{3} \end{pmatrix} = \delta_{J_{1}, J_{3}} \delta_{J_{2}, J_{4}} \delta_{m_{1}, m_{1}} \delta_{m_{2}, m_{2}} \delta_{m_{3}, m_{3}}
$$

(A.6)

$$
\sum_{J_{3} J_{4} J_{5}} (2 J_{3} + 1) \begin{pmatrix} J_{1}, J_{2}, J_{3} \end{pmatrix} \begin{pmatrix} J_{1}, J_{2}, J_{3} \end{pmatrix} = \delta_{J_{1}, J_{3}} \delta_{J_{2}, J_{4}} \delta_{m_{1}, m_{1}} \delta_{m_{2}, m_{2}} \delta_{m_{3}, m_{3}} \delta_{J_{1}, J_{2}, J_{3}}
$$

(A.7)

The normalization chosen here is

$$
T_{2} T_{kq} (J_{1}, J_{2}) T_{K}^{+}, (J_{3}, J_{4}) = \delta_{J_{1}, J_{3}} \delta_{J_{2}, J_{4}} \delta_{K, K'} \delta_{Q, Q'}
$$

(A.8)

so choose $\langle \mathcal{J} \parallel T(K) \parallel \mathcal{J}' \rangle = \sqrt{\frac{2 \; K + 1}{2 \; J + 1}}$. Care must be taken when using other references. For example, Martin and Spearman\(^{54}\) have the following normalization relationship for the $T_{kq}$'s with total angular momentum $\mathcal{J}$:

$$
T_{2} T_{kq}, T_{K}^{+} = \frac{2 \; J + 1}{2 \; K + 1} \delta_{K, K'} \delta_{Q, Q'}
$$

Once the normalization is defined and therefore the reduced matrix element known, $T_{kq} (\mathcal{J} \mathcal{J})$ becomes
One can invert this relationship to show, using (A.6)

\[ |JM \times J'M'| = \sum_{KQ} T_{KQ} (J J') (-)^{J - M} \left( \begin{array}{c} J \ K \\ -M \ Q \end{array} \right) \sqrt{2K + 1} \]  

(A.10)

Using the symmetry properties of the 3-J symbol, one finds

\[ \sum_{KQ} T_{KQ} (J J') = (-)^{J_1 - J_2 - Q} \sum_{KQ} T_{KQ} (J_2 J_1) \]  

(A.11)

The identity element is found from its definition

\[ I(J) = \sum_{JM} |JM \times JM| \]

By noting Edmonds (3.7.9)

\[ \left( \begin{array}{c} J \ J' \ 0 \\ M \ -M' \ 0 \end{array} \right) = (-)^{J - M} \frac{\delta_{J J'} \delta_{MM'}}{\sqrt{2J + 1}} \]  

(A.12)

and using (A.7), one finds

\[ I(J) = \sqrt{2J + 1} \sum_{00} T_{00} (J J) \]  

(A.13)

Now that the basic properties are known, it would be useful to find more complicated properties. First consider finding the trace of any number of \( T_{KQ} \)'s. The trace of one \( T_{KQ} \) is
The trace of the product of two $T_{kq}$'s is given by equation (A.8). In order to find traces of more than two $T_{kq}$'s multiplied together, one must eventually reduce the number of $T_{kq}$'s to two $T_{kq}$'s so that (A.8) may be used. It is therefore necessary to know how to express a product of two $T_{kq}$'s in terms of the basis set \{ $T_{kq}(j_3')$ \}.

\[
T_{kq}(j_1j_2) = T_{kq}(j_1j_2) I(j) = \sum \delta_{k_1k_2} \delta_{q_1q_2} (A.14)
\]

To find this, express each of the $T_{kq}$'s on the left hand side in terms of standard notation using (A.9). Then use (A.10) and the following formula from Edmonds to reconstruct the right hand side in terms of the $T_{kq}$'s:

\[
T_{kq}(j_1j_2) T_{kq}(j_3j_4) = \sum_{KQ} \delta_{k_2k_3} \delta_{q_2q_3} (2J_z + [J_1 - J_4 + Q])
\]

(A.15)

One can therefore reexpress any product of $T_{kq}$'s in terms of a lesser number of them by repeated application of (A.15).
Another desired correspondence is that relating \( T_{KQ} \)'s to constituent \( T_{KQ} \)'s when the total angular momentum is a sum of angular momenta. For example, if \( \vec{F} = \vec{I} + \vec{J} \), then

\[
T_{KQ}(F,F_z) = (-)^{\phi} \sum_{\lambda_z \phi_z} T_{k, \phi_z}(I,I_z) T_{k_z \phi_z}(J,J_z) \times \\
\frac{1}{\sqrt{(2F+1)(2F_z+1)(2\lambda_z+1)(2\lambda_{z'}+1)(2K+1)}} \begin{pmatrix} \lambda, \lambda_z, K \\ q_z, q_z', Q \end{pmatrix} \begin{pmatrix} I_z, J_z, F_z \\ I, J, F \end{pmatrix}
\]  
(A.17)

and conversely

\[
T_{k, \phi_z} (I, I_z) T_{k_z \phi_z} (J, J_z) = \sum_{KQF,F_z} (-)^{\phi} \frac{1}{\sqrt{(2F+1)(2F_z+1)(2\lambda_z+1)(2\lambda_{z'}+1)(2K+1)}} \times \\
\times T_{KQ}(F,F_z) \begin{pmatrix} \lambda, \lambda_z, K \\ q_z, q_z', Q \end{pmatrix} \begin{pmatrix} I_z, J_z, F_z \\ I, J, F \end{pmatrix}
\]  
(A.18)

where \( \phi = [F_z + K - F] + [I_z - J, -I_z + J_z + Q] \) in both (A.17) and (A.18).

The derivation of (A.17) relies upon the fact that

\[
|FM\rangle = \sum_{m_x m_y} |m_x m_y \rangle \langle m_x m_y | FM\rangle
\]

\[
|m_x m_y\rangle = \sum_{FM} |FM\rangle \langle FM| m_x m_y \rangle
\]

with

\[
\langle m_x m_y | FM \rangle = \langle FM | m_x m_y \rangle = (-)^{I-x+F+y} \sqrt{2F+1} \begin{pmatrix} I & J & F \\ m_x & m_y & -m \end{pmatrix}
\]  
(A.19)
Also used in the derivation was the following relationship from Brink and Satchler:

\[
\begin{pmatrix}
J_{13} & J_{24} & J \\
m_{13} & m_{24} & m
\end{pmatrix}
\begin{pmatrix}
J_{1} & J_{2} & J_{13} \\
m_{1} & m_{2} & m_{13}
\end{pmatrix}
\begin{pmatrix}
J_{3} & J_{4} & J_{34} \\
m_{3} & m_{4} & m_{34}
\end{pmatrix}
\]

\begin{align}
\sum_{J_{13}J_{24}J} & \delta_{J_{13}J_{1}} \delta_{J_{24}J_{2}} \\
\times & \begin{pmatrix}
J_{1} & J_{2} & J_{13} \\
m_{1} & m_{2} & m_{13}
\end{pmatrix}
\begin{pmatrix}
J_{3} & J_{4} & J_{34} \\
m_{3} & m_{4} & m_{34}
\end{pmatrix}
\end{align}

\( (A.20) \)

By using (A.6) and the 9-J orthogonality relationship from Edmonds (A.21) on (A.17), one gets (A.18).

\[
\sum_{J_{13}J_{24}J} \prod_{j} \begin{pmatrix}
J_{j1} & J_{j2} & J \\
m_{j1} & m_{j2} & m_{j}
\end{pmatrix}
\begin{pmatrix}
J_{j3} & J_{j4} & J_{j34} \\
m_{j3} & m_{j4} & m_{j34}
\end{pmatrix}
\]

\( (A.21) \)

Again assuming that \( \vec{F} = \vec{F} + \vec{J} \), many times it is useful to know how to express these angular momentum operators in terms of the \( T_{K_A} \)'s as they appear in the Hamiltonian of the system. Therefore consider the following four operators: \( \vec{F}, \vec{F}, \vec{J}, \text{ and } \vec{F} \cdot \vec{J} \). The coordinate system used is the spherical tensor coordinate system as these naturally yield the spherical tensor operators.

\[
\hat{C} \pm_1 = \vec{F} \pm \frac{\hat{e}_x \pm i \hat{e}_y}{\sqrt{2}}
\]

\( (A.22) \)

\[
\hat{C} \phi_0 = \hat{C}_z
\]

Then

\[
\hat{C}^* \cdot \hat{C}_j = \delta_{ij} , \quad \hat{C}^* = (-)^i \hat{C}_{-i}
\]

\( (A.23) \)
A vector operator $\vec{A}$ can then be expanded as

$$\vec{A} = \sum_q \hat{e}_q^* \vec{A}_q$$

with $\vec{A}_q = \hat{e}_q \cdot \vec{A}$  \hspace{1cm} (A.24)

Since the particular angular momentum operators are themselves spherical tensor operators, then one can use the Wigner-Eckart theorem (A.5) to find the matrix elements. For example

$$\langle F' \parallel \hat{T}_F \parallel F \rangle = \delta_{F,F'} \frac{\sqrt{F(F+1)(2F+1)}}{\sqrt{F'(F'+1)(2F'+1)}}$$

\hspace{1cm} (A.25)

From Edmonds

$$\langle F' \parallel \hat{T}_F \parallel F \rangle = \delta_{F,F'} \frac{\sqrt{F(F+1)(2F+1)}}{\sqrt{F'(F'+1)(2F'+1)}}$$

\hspace{1cm} (A.26)

So, using (A.7) and (A.10), one finds

$$\vec{F'} = \sum_q \hat{e}_q^* \left( F \parallel \hat{T}_{q'q} \parallel F \right) \left( \sqrt{F(F+1)(2F+1)} \right)$$

\hspace{1cm} (A.27)

Similarly, $\vec{T} \cdot \vec{F}$ is

$$\vec{T} \cdot \vec{F} = \frac{1}{2} \left[ \hat{T}^2 - \hat{T} \cdot \hat{J} \cdot \hat{J} \right]$$

\hspace{1cm} (A.28)

To find $\vec{T}$ and $\vec{F}$, one must know how to find their reduced matrix elements. To do this, one needs one of the following two formulas from Edmonds:
For $\mathcal{T}(k)$ acting only on part 1 of a compound system

$$< r', r_j, j_z, J' || \mathcal{T}(k) || r', j_z, J > = (-)^{J_j + J_z + J' + K} *$$

$$* \frac{1}{7(2J'+1)(2J+1)} \left\{ \begin{array}{c}
J'_j, J'_z, J' \\
J, j_z, K
\end{array} \right\} < r', J' || \mathcal{T}(k) || r', j_z, J >$$

or for $\mathcal{T}(k)$ acting only on part 2 of a compound system

$$< r', r_j, j_z, J' || \mathcal{T}(k) || r', j_z, J > = (-)^{J_j + J_z + J' + K} *$$

$$* \frac{1}{7(2J'+1)(2J+1)} \left\{ \begin{array}{c}
J'_j, J'_z, J' \\
J, j_z, K
\end{array} \right\} < r', J' || \mathcal{T}(k) || r', j_z, J >$$

Following the same method as was indicated in the derivation of (A.27), one finds for $\mathcal{I}'$ and $\mathcal{J}'$:

$$\mathcal{I}' = \mathcal{I} \otimes \mathcal{I}(J) = \sum \delta^* \delta \ T_{q} (FF') \frac{< F || \mathcal{I} || F >}{\sqrt{3}}$$

$$= \sum \delta^* \delta \ \Sigma (\frac{1}{q} \ T_{q} (FF') \left\{ \begin{array}{c}
J \ F' \ I \\
F \ J \ I
\end{array} \right\} \frac{(2J'+1)(2J+1)(2J+1)}{3}$$

and

$$\mathcal{J}' = \mathcal{J} \otimes \mathcal{J}(F) = \sum \delta^* \delta \ \Sigma (\frac{1}{q} \ T_{q} (FF') \left\{ \begin{array}{c}
J \ F' \ I \\
F \ J \ I
\end{array} \right\} \frac{(2J'+1)(2J+1)(2J+1)}{3}$$
The remaining formulas in this appendix will just be stated as they are taken from other sources. First, when one of the angular momenta is zero, several of the formulas will simplify. To see this one needs (A.12) for the 3-J symbol,

\[
\begin{pmatrix} J_1 & J_2 & J_3 \\ 0 & J_3 & J_2 \end{pmatrix} = \frac{(-)^{J_1+J_2+J_3}}{(2J_2+1)(2J_3+1)}
\]

(A.33)

for the 6-J symbol and

\[
\begin{pmatrix} J & J & 0 \\ J_1 & J_2 & J_3 \end{pmatrix} = \frac{(-)^{J_2+J_3+J+J}}{(2J+1)(2J+1)} \begin{pmatrix} J_4 & J_3 & J \\ J_1 & J_2 & J \end{pmatrix}
\]

(A.34)

for the 9-J symbol.

Useful in the derivation of the $P_{\vec{e}x}$ operator is the following formula from Brink and Satchler:

\[
\bar{\xi} (-)^{2\ell} (2\ell+1) \begin{pmatrix} J_1 & J_2 & \ell \\ J_1 & J_2 & J \end{pmatrix} = 1
\]

(A.35)

Also used in the body of the text are the following sum formulas for the 6-J symbols:

\[
\begin{pmatrix} J_1 & J_2 & J_{12} \\ J_3 & J_{23} & J_2 \end{pmatrix} \begin{pmatrix} J_{23} & J_1 & J_{123} \\ J_4 & J_1 \end{pmatrix} = \sum (-)^{J_1+J_2+J_3+J_4+J+J+J+J_{123}+J_2} \quad \star
\]

(A.36)
In conclusion it should be noted that when the two arguments of the $T_{kQ}'s$ are the same, they can be expressed in terms of that angular momentum to give the standard multipole operators from quantum mechanics. These relationships are given in Table A.1 taken from Ambler, Eisenstein and Schooley for the first few orders. Their papers also indicate how to take the trace of products of angular momentum matrices. Note that the entire table can be constructed by assuming that

$$
\sum_{\ell} (2\ell+1)(2\ell''+1) \begin{bmatrix} \ell, \ell_2 \ell \end{bmatrix} \begin{bmatrix} \ell, \ell_2 \ell \end{bmatrix} = \delta_{\ell''} \ell''
$$

(A.37)

Other useful angular momentum formulas can be found in the standard texts mentioned in the beginning. Tables of 3-J and 6-J symbols as well as a summary of basic formulas can be found in the book by Rotenberg, Bivins, Metropolis, and Wooten. A few of the $T_{kQ}$ formulas can be found
| $y_{10}$ | $\frac{1}{2} (\frac{3}{2\pi})^{\frac{1}{2}} z$ |
| $y_{11}$ | $\mp \frac{1}{2} (\frac{3}{2\pi})^{\frac{1}{2}} (x + iy)$ |
| $y_{12}$ | $\frac{1}{2} (\frac{3}{2\pi})^{\frac{1}{2}} (x + iy)^2$ |
| $y_{20}$ | $\frac{1}{4} (\frac{3}{2\pi})^{\frac{1}{2}} (3x^2 - r^2)$ |
| $y_{21}$ | $\mp \frac{1}{4} (\frac{3}{2\pi})^{\frac{1}{2}} (2x)(x + iy)$ |
| $y_{22}$ | $\frac{1}{4} (\frac{3}{2\pi})^{\frac{1}{2}} (x + iy)^3$ |
| $y_{30}$ | $\frac{1}{4} (\frac{3}{2\pi})^{\frac{1}{2}} (5x^2 - 3x^2 - r^2)$ |
| $y_{31}$ | $\mp \frac{1}{8} (\frac{3}{2\pi})^{\frac{1}{2}} (5x^2 - r^2)(x + iy)$ |
| $y_{32}$ | $\frac{1}{8} (\frac{3}{2\pi})^{\frac{1}{2}} (x + iy)^2$ |
| $y_{33}$ | $\mp \frac{1}{8} (\frac{3}{2\pi})^{\frac{1}{2}} (x + iy)^3$ |

$T_{10} (\mathbf{J})$ (Normalisation $Q_0$)

- $a_0 \cdot 1$
- $a_1 \mathbf{J}_2$
- $\mp a_1 (\frac{1}{8\pi}) \mathbf{J}_2$
- $a_2 \{3 \mathbf{J}_z^2 - \mathbf{J}(\mathbf{J} + 1)\}^2$
- $\mp (\frac{1}{8})^{\frac{1}{2}} a_2 \{ \mathbf{J}_x \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_x \}^2$
- $\frac{1}{4} a_2 (\mathbf{J}_z^2)$
- $a_3 \{5 \mathbf{J}_z^3 - 3 \mathbf{J}_z \mathbf{J}(\mathbf{J} + 1) + \mathbf{J}_z\}^2$
- $\mp (\frac{1}{8})^{\frac{1}{2}} a_3 \{4 \mathbf{J}_z \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_z\} + (\mathbf{J}_z^2 \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_z + \mathbf{J}_z^2 \mathbf{J}_z)^2$
- $(\frac{1}{8})^{\frac{1}{2}} a_3 \{ \mathbf{J}_x \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_x \} + (\mathbf{J}_z^2 \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_z + \mathbf{J}_z \mathbf{J}_z + \mathbf{J}_z^2 \mathbf{J}_z)^2$
- $\mp (\frac{1}{8})^{\frac{1}{2}} a_3 \{ \mathbf{J}_z^3 \}$

**Table A.1**
in Rose\textsuperscript{58} and in Appendix A of a paper by Happer and Mathur\textsuperscript{59} in the notation of Rose\textsuperscript{60}.
APPENDIX B

SECULAR APPROXIMATION

Many times in physics the energy E of an atom due to its Hamiltonian alone is so much greater than that due to relaxation effects, $\frac{1}{\tau}$, that terms on the order of $\frac{1}{\tau^2}$ can be judiciously dropped from the differential equation governing the time development of various operators.

For example, since the density matrix is an ordered set of numbers, one can write its matrix elements in the form of a vector. The equation for the time development of the density matrix is a first order differential equation. Therefore consider the time development of a vector $|\chi(t)\rangle$ which obeys the following equation

\[
\frac{d}{dt} |\chi(t)\rangle = \mathcal{A}(t) |\chi(t)\rangle
\]  

(B.1)

A scalar derivation of the physical meaning of the secular approximation is given in Appendix I of Barrat and Cohen-Tannoudji's paper. Assume that in some sense (to be shown in equation (B.17)) that the time dependent part of $\mathcal{A}(t)$ contributes a small amount so that $\mathcal{A}$ can be written as

\[
\mathcal{A}(t) = \mathcal{A}_0 + \lambda \mathcal{B}(t)
\]  

(B.2)

where $\mathcal{A}_0$ is the time independent part of $\mathcal{A}$ and $\lambda$ represents
the "size" associated with \( B(t) \). To find \( |x(t)\rangle \), expand it in terms of powers of \( \lambda \) and solve by iteration.

\[
|x(t)\rangle = \sum_{n=0}^{\infty} \lambda^n |x(t)\rangle_n
\]  

(B.3)

So, to zeroth order

\[
\frac{d}{dt} |x(t)\rangle_0 = A_0 |x(t)\rangle_0
\]  

(B.4)

Assume that \( A_0 \) can be diagonalized so that

\[
A_0 |\alpha\rangle = \alpha |\alpha\rangle
\]  

(B.5)

Then

\[
\frac{d}{dt} |x(t)\rangle_0 = \sum_{\alpha} |\alpha\rangle \langle \alpha | x(t)\rangle_0
\]  

(B.6)

If the inner product of (B.6) is taken with \( |\beta\rangle \), one finds

\[
\frac{d}{dt} \langle \beta | x(t)\rangle_0 = \beta \langle \beta | x(t)\rangle_0
\]  

(B.7)

The solution of (B.7) is

\[
\langle \beta | x(t)\rangle_0 = e^{\beta t} \langle \beta | x(0)\rangle_0
\]  

(B.8)

Since the zeroth order solution is now known, the first order solution can be found in terms of it:
\[
\frac{d}{dt} \langle x(t) \rangle_i = A_0 \langle x(t) \rangle_i + B(t) \langle x(t) \rangle_0
\]  
(B.9)

Taking the inner product of (B.9) with \( \langle \alpha \rangle \) results in

\[
\frac{d}{dt} \langle \alpha 1 x(t) \rangle_i = \alpha \langle \alpha 1 x(t) \rangle_i + \langle \alpha 1 B(t) 1 x(t) \rangle_0
\]  
(B.10)

\[
= \alpha \langle \alpha 1 x(t) \rangle_i + \sum_\beta \langle \alpha 1 B(t) 1 \beta \rangle \langle \beta 1 x(t) \rangle_0
\]

where the fact that \( \langle \alpha 1 A_0 1 x(t) \rangle_i = \sum_\beta \langle \alpha 1 A_0 \beta \rangle \langle \beta 1 x(t) \rangle_i = \alpha \langle \alpha 1 x \rangle_i \) (B.11) has been utilized.

So

\[
\mathcal{L} \frac{d}{dt} \left[ e^{-\lambda t} \langle \alpha 1 x(t) \rangle_i \right] = \sum_\beta \langle \alpha 1 B(t) 1 \beta \rangle \langle \beta 1 x(t) \rangle_0
\]  
(B.12)

or, using (B.8)

\[
\langle \alpha 1 x(t) \rangle_i = \mathcal{L} \left\{ \langle \alpha 1 X(0) \rangle_i + \langle \alpha 1 B(t) 1 \beta \rangle \int_0^t dt' e^{(B-\alpha) t'} \langle \beta 1 X(t') \rangle_0 \right\}
\]  
(B.13)

To evaluate the integral, assume that \( B(t) \) can be expanded in a Fourier series with no \( n=0 \) term as the constant part of \( A(t) \) was relegated to \( A_0 \).

\[
B(t) = \sum_{n=-\infty}^{\infty} B_n e^{i\omega n t}
\]  
(B.14)
The prime on the summation sign indicates the lack of an \( n=0 \) term. Using B.14) in (B.13,) one finds

\[
\langle \alpha | X(t) \rangle = \mathcal{L} \left\{ \langle \alpha | X(0) \rangle + \sum_{\beta} \langle \beta | X(0) \rangle \sum_{n} \langle \alpha | B_{n} \rangle \left( \frac{e^{(\beta - \alpha + i \omega) t}}{\beta - \alpha + i \omega} - 1 \right) \right\} + \sum_{\beta} \sum_{n} \langle \beta | X(0) \rangle \langle \alpha | B_{n} \rangle \lambda \left( \frac{e^{(\beta - \alpha + i \omega) t}}{\beta - \alpha + i \omega} - 1 \right) \tag{B.15}
\]

Inclusion of both the zeroth order and first order in \( lx(\tau) \) gives

\[
\langle x(t) \rangle = \mathcal{L} \left\{ \langle \alpha | X(0) \rangle + \sum_{\beta} \langle \beta | X(0) \rangle \sum_{n} \langle \alpha | B_{n} \rangle \lambda \left( \frac{e^{(\beta - \alpha + i \omega) t}}{\beta - \alpha + i \omega} - 1 \right) \right\} \tag{B.16}
\]

The secular approximation consists of saying that

\[
\left| \frac{\lambda}{\beta - \alpha + i \omega} \right| << 1 \tag{B.17}
\]

Since \( \omega \) cannot equal zero and \( \alpha \) can equal \( \beta \) for (B.17) to be true for all terms, \( \omega \) must be large compared to the other time constants in the problem, which have the same order of magnitude as \( \lambda \). For example, in equation (3.44) \( \lambda \) can be associated with \( \frac{\tau}{\gamma} \) and \( \omega \) with differences of hyperfine or Zeeman frequencies. Since the hyperfine frequency is on the order of \( 10^{10} \) Hz., and the Zeeman frequency is on the order of \( 10^{6} \) Hz., the secular approximation can be used since \( \frac{\tau}{\gamma} \) turns out to be less than the order of 100 Hz. The same argument holds for the derivation of equation (3.98).