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Introduction

The basic idea of optical pumping [1], for which Kastler [2] received the 1966 Nobel Prize in physics, is that the photons in a beam of light can transfer order to atoms or molecules by scattering. Originally the term “optical pumping” referred to ordering the spin degrees of freedom. More recently, optical pumping has been widely used to order the translational as well as the spin degrees of freedom for cooling and trapping experiments.

Optical pumping experiments can be quite simple and inexpensive and still yield precise spectroscopic information. They can also be quite intricate and require substantial resources. Optical pumping is a fascinating area of study in its own right, but in addition it has many applications (clocks, magnetometers, quantum optics, spin-polarized nuclei) where the central focus is elsewhere. We will assume that the reader of this book already has a basic understanding of quantum mechanics, atomic physics, optics, and magnetic resonance. There are many excellent books that discuss these issues. Familiarity with linear algebra, complex analysis, Fourier and Laplace transforms, and the quantum theory of angular momentum would be helpful for following some of the mathematics in this book.

Because real atoms can have a large number of spin sublevels, because the optical interactions, especially at low buffer-gas pressures, depend in a detailed way on the spectral profile and polarization of the light, and because of the complicated collisional relaxation mechanisms, realistic numerical modeling of optically pumped atoms is a computational challenge. Consequently, the system is often represented with models [3–5] that consider only a few spin sublevels and greatly simplify the physics of optical pumping and spin relaxation. Such simplified models can be valuable for conceptual insights and can give results in qualitative agreement with observations. A major aim of this book is to show that modern scientific computing software makes it practical to analyze the full, multilevel system of optically pumped atoms under most experimental conditions, for example, magnetic resonance with one or more oscillating magnetic fields, coherent-Raman-scattering (coherent population trapping) resonances induced by modulated light, magneto-optical forces on multilevel atoms, and various spin-relaxation processes. To make most effective use of contemporary mathematical software, it is especially useful to analyze optical pumping situations in the Liouville space of density matrices, ρ , rather than in the traditional Schrödinger (Hilbert) space of wave functions.

Liouville space has long been used, either explicitly or implicitly, to analyze physics like that of optical pumping. A good general introduction to Liouville space from a viewpoint similar to ours can be found in the book *Principles of Magnetic Resonance in One and Two Dimensions*, by Ernst *et al.* [6]. Another good introduction with more emphasis on lasers is *The Liouville Space Formalism in Atomic Spectroscopy*, by Schuller [7]. The focus of our book on aspects of Liouville space that are particularly well adapted to computer programming appears to be unique.

To make the discussion of the book less abstract, we have illustrated key points with sections of MATLAB code, which can be assembled to generate fairly sophisticated programs. We have tried to write the codes for brevity and maximum clarity, not for maximum speed. Many sections of code will run much faster with minor modifications. Analogous code can be written for other scientific-computing software, for example, Mathematica. Some familiarity with scientific-computing software would be helpful to a reader interested in writing specialized programs based on these illustrative codes. The codes can be downloaded from <http://minds.wisconsin.edu/handle/1793/35675>

Wherever possible, we have tried to use traditional symbols for familiar physical quantities. Regrettably, this means that we use the same symbols to represent quite different physical quantities, for example, E for the energy or for the amplitude of the electric field, ρ for electric charge density or for the density matrix of quantum mechanics, and S for the electric spin quantum number or for the Poynting vector (electromagnetic energy flux). Wherever the context is sufficient to make the meaning of the symbol clear, we have avoided introducing new fonts, superscripts, or subscripts to resolve the ambiguity.

An Example Some of the most important ideas of Liouville space can be illustrated by the familiar example of the hypothetical spin-1/2 atom shown in Figure 1.1. The probability of finding the atom in sublevel $|\alpha\rangle$ with azimuthal quantum number $m_S = \alpha = +1/2$ is $\rho_{\alpha\alpha} = 1/2 + \langle S_z \rangle$ and the probability of finding the atom in sublevel $|\beta\rangle$ with $m_S = \beta = -1/2$ is $\rho_{\beta\beta} = 1/2 - \langle S_z \rangle$. Here $\langle S_z \rangle$ is the expectation value of the longitudinal spin of the atom. The off-diagonal elements (coherences) of the density matrix, $\rho_{\alpha\beta} = \langle S_x - iS_y \rangle$ and $\rho_{\beta\alpha} = \langle S_x + iS_y \rangle$, describe transverse components of the spin. For the conditions outlined in the caption of Figure 1.1, the elements of the density matrix change at the rates

$$\begin{aligned} \frac{d}{dt}\rho_{\alpha\alpha} &= 2f\Gamma_p\rho_{\beta\beta} - \frac{\Gamma_c}{2}(\rho_{\alpha\alpha} - \rho_{\beta\beta}) - \frac{\omega}{2}(\rho_{\beta\alpha} + \rho_{\alpha\beta}), \\ \frac{d}{dt}\rho_{\beta\alpha} &= -(\Gamma_p + \Gamma_c)\rho_{\beta\alpha} + \frac{\omega}{2}(\rho_{\alpha\alpha} - \rho_{\beta\beta}), \\ \frac{d}{dt}\rho_{\alpha\beta} &= -(\Gamma_p + \Gamma_c)\rho_{\alpha\beta} + \frac{\omega}{2}(\rho_{\alpha\alpha} - \rho_{\beta\beta}), \\ \frac{d}{dt}\rho_{\beta\beta} &= -2f\Gamma_p\rho_{\beta\beta} + \frac{\Gamma_c}{2}(\rho_{\alpha\alpha} - \rho_{\beta\beta}) + \frac{\omega}{2}(\rho_{\beta\alpha} + \rho_{\alpha\beta}). \end{aligned} \quad (1.1)$$

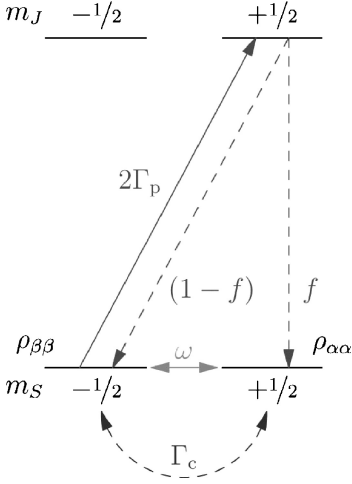


Figure 1.1 Pumping of a hypothetical alkali-metal atom with no nuclear spin. The quantization (z) axis is defined by the propagation direction of a circularly polarized light beam that pumps atoms out of the ground-state sublevel with $m_S = \beta = -1/2$ at a rate $2\Gamma_p$. The light is weak enough for stimulated emission of excited atoms to be neglected. Owing to spontaneous radiative emission and quenching collisions, a fraction f

of excited atoms decays to the sublevel with $m_S = \alpha = +1/2$, and the remaining fraction returns to the initial sublevel. For pure spontaneous emission we would have $f = 1/3$. Spin-changing collisions damp the ground-state spin polarization at the rate Γ_c . An externally applied magnetic field causes the ground-state atoms to rotate about the y axis at rate ω .

We can group the elements $\rho_{\mu\nu}$ as a 2×2 matrix, ρ , in Schrödinger space

$$\rho = \begin{bmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{bmatrix} = \sum_{\mu\nu} |\mu\rangle\langle\nu| \rho_{\mu\nu}, \quad (1.2)$$

or as a 4×1 column vector, $|\rho\rangle$, in Liouville space

$$|\rho\rangle = \begin{bmatrix} \rho_{\alpha\alpha} \\ \rho_{\beta\alpha} \\ \rho_{\alpha\beta} \\ \rho_{\beta\beta} \end{bmatrix} = \sum_{\mu\nu} |\mu\nu\rangle \rho_{\mu\nu}. \quad (1.3)$$

The column vector $|\rho\rangle$ of (1.3) is formed from the matrix ρ of (1.2) by placing each column of ρ below the one to its left.

Bases The basis matrices $|\mu\rangle\langle\nu|$ of the expansion (1.2) are

$$\begin{aligned} |\alpha\rangle\langle\alpha| &= \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, & |\beta\rangle\langle\alpha| &= \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}, \\ |\alpha\rangle\langle\beta| &= \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, & |\beta\rangle\langle\beta| &= \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}, \end{aligned} \quad (1.4)$$

and the basis vectors of the expansion (1.3) are

$$\begin{aligned} |\alpha\alpha\rangle &= \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, & |\beta\alpha\rangle &= \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \\ |\alpha\beta\rangle &= \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, & |\beta\beta\rangle &= \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \end{aligned} \quad (1.5)$$

In accordance with the ordering convention of (1.2) and (1.3) we can denote the transformation of a basis matrix to a basis vector by

$$|\mu\nu\rangle = | |\mu\rangle \langle \nu| \rangle. \quad (1.6)$$

Expansion Amplitudes The expansion amplitudes of (1.2) can be written as

$$\rho_{\mu\nu} = \text{Tr} \left[(|\mu\rangle \langle \nu|)^\dagger \rho \right] = \langle \mu | \rho | \nu \rangle. \quad (1.7)$$

Similarly, the expansion amplitudes of (1.3) can be written as

$$\rho_{\mu\nu} = \langle \mu \nu | \rho \rangle, \quad (1.8)$$

where the row vectors, $\langle \mu \nu | = | \mu \nu \rangle^\dagger$, are

$$\begin{aligned} \langle \alpha\alpha | &= [1 \ 0 \ 0 \ 0], \\ \langle \beta\alpha | &= [0 \ 1 \ 0 \ 0], \\ \langle \alpha\beta | &= [0 \ 0 \ 1 \ 0], \\ \langle \beta\beta | &= [0 \ 0 \ 0 \ 1]. \end{aligned} \quad (1.9)$$

In MATLAB, the coding statement to generate the column vector `crho`, representing $|\rho\rangle$ of (1.3), from `rho`, representing ρ of (1.2), is

Code 1.1

```
crho = rho(:)
```

The inverse coding statement, to convert the column vector `crho` back to a 2×2 matrix, is

Code 1.2

```
rho = reshape(crho,2,2)
```

The Damping Matrix We can write (1.1) as the matrix equation

$$\frac{d}{dt}|\rho\rangle = -G|\rho\rangle. \quad (1.10)$$

The damping matrix is

$$\begin{aligned} G &= \Gamma_p A_p + \Gamma_c A_c + i\omega S_y^\odot \\ &= \frac{1}{2} \begin{bmatrix} \Gamma_c & \omega & \omega & -4f\Gamma_p - \Gamma_c \\ -\omega & 2\Gamma_p + 2\Gamma_c & 0 & \omega \\ -\omega & 0 & 2\Gamma_p + 2\Gamma_c & \omega \\ -\Gamma_c & -\omega & -\omega & 4f\Gamma_p + \Gamma_c \end{bmatrix}. \end{aligned} \quad (1.11)$$

The symbols A_p , A_c , and S_y^\odot represent “superoperators” for Liouville space. The superoperators that account for optical pumping and damping are

$$A_p = \begin{bmatrix} 0 & 0 & 0 & -2f \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 2f \end{bmatrix} \quad (1.12)$$

and

$$A_c = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & -1 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ -1 & 0 & 0 & 1 \end{bmatrix}. \quad (1.13)$$

The y component of the Liouville-space spin operator, a “commutator superoperator” that we will discuss in more detail below, is

$$S_y^\odot = \frac{1}{2i} \begin{bmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{bmatrix}. \quad (1.14)$$

In the body of this book, we will discuss systematic ways to generate superoperators such as A_p , A_c , and S_y^\odot .

Alternative Basis Instead of using the simple basis matrices of (1.4), we will often find it convenient to use other linearly independent (but not necessarily orthonormal) bases. For example, we can use unit matrix $1^{\{S\}}$ and the spin operators,

$$\begin{aligned} 1^{\{S\}} &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, & S_x &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \\ S_y &= \frac{1}{2i} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}, & S_z &= \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \end{aligned} \quad (1.15)$$

In analogy to (1.2) and (1.3), the column-vector equivalents of the matrices in (1.15) are

$$\begin{aligned} |1^{\{S\}}\rangle &= \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}, & |S_x\rangle &= \frac{1}{2} \begin{bmatrix} 0 \\ 1 \\ 1 \\ 0 \end{bmatrix}, \\ |S_y\rangle &= \frac{1}{2i} \begin{bmatrix} 0 \\ -1 \\ 1 \\ 0 \end{bmatrix}, & |S_z\rangle &= \frac{1}{2} \begin{bmatrix} 1 \\ 0 \\ 0 \\ -1 \end{bmatrix}. \end{aligned} \quad (1.16)$$

The Hermitian conjugate row vectors corresponding to (1.16) are

$$\begin{aligned} \langle 1^{\{S\}}| &= |1^{\{S\}}\rangle^\dagger = [1 \quad 0 \quad 0 \quad 1], \\ \langle S_x| &= |S_x\rangle^\dagger = \frac{1}{2} [0 \quad 1 \quad 1 \quad 0], \\ \langle S_y| &= |S_y\rangle^\dagger = \frac{1}{2i} [0 \quad 1 \quad -1 \quad 0], \\ \langle S_z| &= |S_z\rangle^\dagger = \frac{1}{2} [1 \quad 0 \quad 0 \quad -1]. \end{aligned} \quad (1.17)$$

We see that the total probability of finding the atom in some ground-state sublevel is

$$\text{Tr}[1^{\{S\}}\rho] = \rho_{aa} + \rho_{\beta\beta} = \langle 1^{\{S\}}|\rho\rangle. \quad (1.18)$$

In (1.18) we have assumed that the pumping rate Γ_p is so small compared with the spontaneous decay rate and collisional quenching rates of the excited atoms that the probability of finding atoms in the excited state is negligibly small, and we can write

$$\langle 1^{\{S\}}|\rho\rangle = 1. \quad (1.19)$$

The expectation value of the longitudinal spin S_z of the atom is

$$\langle S_z\rangle = \text{Tr}[S_z\rho] = \frac{1}{2}(\rho_{aa} - \rho_{\beta\beta}) = \langle S_z|\rho\rangle. \quad (1.20)$$

In like manner, we find $\langle S_x\rangle = \langle S_x|\rho\rangle$ and $\langle S_y\rangle = \langle S_y|\rho\rangle$. The expectation value of an arbitrary (not necessarily Hermitian) operator X is

$$\langle X\rangle = \langle X^\dagger|\rho\rangle. \quad (1.21)$$

Constraints From inspection of (1.11)–(1.14) we see that

$$\begin{aligned} \langle 1^{\{S\}}|A_p &= 0, & \langle 1^{\{S\}}|A_c &= 0, \\ \langle 1^{\{S\}}|S_y^\odot &= 0, & \text{and } \langle 1^{\{S\}}|G &= 0. \end{aligned} \quad (1.22)$$

In view of (1.22) and (1.11), we can multiply (1.10) by $(1^{\{S\}}|$ to find

$$\frac{d}{dt}\text{Tr}[\rho] = \frac{d}{dt}(1^{\{S\}}|\rho) = -(1^{\{S\}}|G|\rho) = 0. \quad (1.23)$$

We see that the constraints (1.22) ensure that the number of atoms neither increases nor decreases as a result of the various evolution mechanisms, pumping, collisional relaxation, or Larmor precession. The evolution described by (1.10) must also keep the density matrix Hermitian. This implies an additional constraint on G that we will discuss in more detail in the body of this book, but which we will outline here. Define a transposition matrix, T , a superoperator that transforms the basis states (1.5) of Liouville space as

$$T|\mu\nu) = |\nu\mu). \quad (1.24)$$

For the example discussed here we have

$$T = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \quad (1.25)$$

We define the Liouville conjugate, G^\ddagger , of a superoperator G by

$$G^\ddagger = T G^* T. \quad (1.26)$$

Here G^* is the complex conjugate of G . As we will discuss in more detail below, in order that the evolution equation (1.10) keep ρ Hermitian we must have

$$G = G^\ddagger. \quad (1.27)$$

The constraints (1.22) and (1.27) on G , and additional constraints that we will mention later, are analogous to the constraint $H = H^\dagger$ for the Hamiltonian H of Schrödinger space, which ensures that the wave function $|\psi\rangle$ changes in a way that keeps $\langle\psi|\psi\rangle = 1$.

Eigenvectors Except for unusual situations of “critical damping”, the damping matrix G of (1.11) will have four linearly independent right (column) eigenvectors, $|\gamma_j\rangle$, and a corresponding set of left (row) eigenvectors, which we denote by $\langle\langle\gamma_j|$. These are defined, aside from normalization factors, by

$$G|\gamma_j) = \gamma_j|\gamma_j) \quad \text{and} \quad \langle\langle\gamma_j|G = \langle\langle\gamma_j|\gamma_j). \quad (1.28)$$

As long as the eigenvectors are linearly independent, we can use them as a basis for Liouville space and we can normalize them such that

$$\langle\langle\gamma_j|\gamma_k) = \delta_{jk}. \quad (1.29)$$

Then we can write the eigenvector expansion of G as

$$G = \sum_j \gamma_j|\gamma_j)\langle\langle\gamma_j|. \quad (1.30)$$

Transients The formal solution of (1.10) is

$$|\rho_t\rangle = e^{-Gt}|\rho_0\rangle. \quad (1.31)$$

Here $|\rho_0\rangle$ is the value of $|\rho\rangle$ at time $t = 0$, and $|\rho_t\rangle$ is the value at time $t \geq 0$. If the atoms are unpolarized at time $t = 0$, we would have

$$\rho_0 = \frac{1}{2}1^{\{S\}}, \quad \text{or} \quad |\rho_0\rangle = \frac{1}{2}|1^{\{S\}}\rangle. \quad (1.32)$$

A MATLAB code that carries out the matrix exponentiation of (1.31) to evaluate the transient response of the model atom is

Code 1.3

```
Gmp=input('Gmp=');%optical pumping rate
Gmc=input('Gmc=');%collisional relaxation rate
f=input('f=');%fractional transfer rate
w=input('w=');%rotation rate about y axis
PS=[1 0; 0 1];%unit operator for Schroedeinger space
cPS=PS(:); rPS=cPS';%column, row vectors from PS
Ap=[0 0 0 -2*f;0 1 0 0;0 0 1 0; 0 0 0 2*f];%pumping operator
Ac=[1 0 0 -1;0 2 0 0;0 0 2 0;-1 0 0 1]/2;%collision operator
%Spin operators in Schroedinger space
Sx=[0 1;1 0]/2; Sy=[0 1;-1 0]/(2*i); Sz=[1 0; 0 -1]/2;
cSx=Sx(:);cSz=Sz(:); rSx=cSx';rSz=cSz';%column, row vectors from Sj
SyC=[0 1 1 0;-1 0 0 1;-1 0 0 1;0 -1 -1 0]/(2*i);%spin superoperator
G=Gmp*Ap+Gmc*Ac+i*w*SyC;%damping superoperator
nt=100; t=linspace(0,5,nt);%sample times
rho=zeros(4,nt);
for k=1:nt
    rho(:,k)=expm(-G*t(k))*cPS/2;
end
clf; plot(t,real(rSz*rho),'b-'); hold on; grid on;
plot(t,real(rSx*rho),'r-'); xlabel('time t');
legend('\langle S_z \rangle', '\langle S_x \rangle');
```

Figure 1.2 shows a representative transient calculated with Code 1.3.

Eigenvector Expansions For situations where G can be written as an eigenvector expansion, we can substitute (1.30) into (1.31) to find

$$|\rho_t\rangle = \sum_j |\gamma_j\rangle \langle \gamma_j | \rho_0 \rangle e^{-\gamma_j t}. \quad (1.33)$$

Here $\langle \gamma_j | \rho_0 \rangle$ is the “weight” of the j th mode at time $t = 0$. The solution is the sum of decaying exponentials with damping rates γ_j that may be complex. For critical damping, when the particular value of some parameter, such as the damping rate or the magnetic field, causes two eigenvalues of G to converge to a common value, γ_c ,

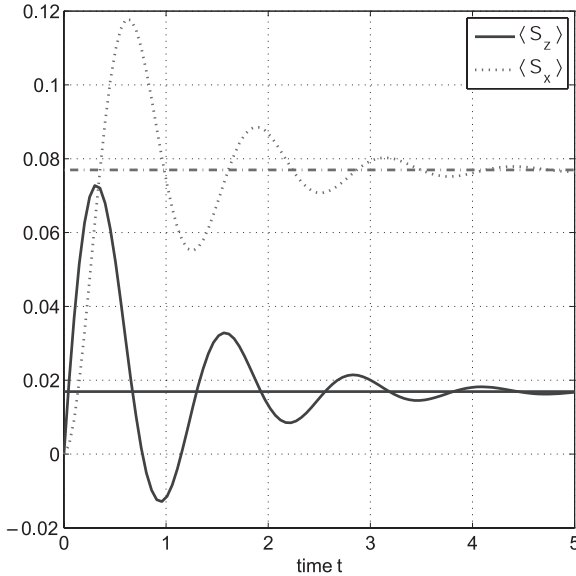


Figure 1.2 Transient calculated with Code 1.3 on page 8 for the parameters $\Gamma_p = 1$, $\Gamma_c = 0.1$, $f = 0.4$, and $\omega = 5$. The horizontal lines are the steady-state spin polarizations calculated with Code 1.5 on page 10.

and when the corresponding right eigenvectors also converge to the same vector, $|\gamma_c\rangle$, there are not enough independent eigenvectors of G to span Liouville space, and the eigenvector expansion (1.30) of G does not exist. This makes no difference if transients are calculated with (1.31), but the expression (1.33) must be revised to include not only a term with the simple exponential time dependence, $e^{-\gamma_c t}$, but also a term with the “critically damped time dependence”, $te^{-\gamma_c t}$. We will discuss critical damping in more detail below.

Steady State For time evolution governed by (1.10), the steady-state solution, $|\rho_\infty\rangle$, is defined by

$$G|\rho_\infty\rangle = 0, \quad (1.34)$$

with

$$(1^{\{S\}}|\rho_\infty\rangle = 1. \quad (1.35)$$

In linear algebra, (1.34) is said to define the null space, $|\rho_\infty\rangle$, of G . With the exception of unusual, multistable conditions, there is a unique steady state for optical pumping problems, so the null space is one-dimensional. Modern mathematical software finds null spaces very efficiently, and when the null space is known to be one-dimensional, even faster algorithms are available. For example, the following MATLAB code `nullfast()` can find the one-dimensional null space more than 10 times faster than the conventional MATLAB built-in routine `null()`.

Code 1.4

```
function [NV invM]= nullfast(M)
K=max(max(abs(M)))*1e-15; warning off;%search the largest matrix element
invM=K*inv(M+K*eye(length(M)));
[i j]=max(sum(invM));%find the dominant matrix column
NV=invM(:,j);%pick up the matrix column as the null vector
NV=NV/sqrt((NV'*NV));%normalize the null vector
```

If the following MATLAB statements are appended to Code 1.3 on page 8 the resulting program will evaluate and plot the steady-state spin polarizations.

Code 1.5

```
rhoin = null(G); rhoin = rhoin/(rPS*rhoin);
plot(t,real(rSz*rhoin)*ones(1,nt),'b-');
plot(t,real(rSx*rhoin)*ones(1,nt),'r-.');
```

Analytic Formulas for Eigenvectors From inspection of (1.34) and (1.28) we see that we can interpret the steady-state solution $|\rho_\infty\rangle$ as the right eigenvector, $|\gamma_1\rangle = |\rho_\infty\rangle$, of G with zero eigenvalue, $\gamma_1 = 0$. From inspection of (1.22) we see that the corresponding left eigenvector is $\langle\gamma_1| = \langle 1^{\{S\}}|$. Solving (1.34) with the matrix G from (1.11), we find that the steady-state mode has the properties

$$\gamma_1 = 0, \quad |\gamma_1\rangle = \frac{1}{2} \left| 1^{\{S\}} + 4aS_x + 4bS_z \right\rangle = \frac{1}{2} \begin{bmatrix} 1 + 2b \\ 2a \\ 2a \\ 1 - 2b \end{bmatrix},$$

$$\langle\gamma_1| = \langle 1^{\{S\}}| = [1 \quad 0 \quad 0 \quad 1]. \quad (1.36)$$

The coefficients a and b are

$$a = \langle S_x \rangle = \frac{f\Gamma_p\omega}{(2f\Gamma_p + \Gamma_c)(\Gamma_p + \Gamma_c) + \omega^2},$$

$$b = \langle S_z \rangle = \frac{f\Gamma_p(\Gamma_p + \Gamma_c)}{(2f\Gamma_p + \Gamma_c)(\Gamma_p + \Gamma_c) + \omega^2}. \quad (1.37)$$

The steady-state solution $|\gamma_1\rangle$ represents an ensemble of atoms with a spin polarization in the zx plane, perpendicular to the axis of rotation (the y axis) of the magnetic field.

Field-Aligned Mode By symmetry it is clear that another mode (eigenvector) must represent spins polarized parallel to the magnetic field. From inspection of (1.11)

we see that

$$\gamma_2 = \Gamma_p + \Gamma_c, \quad |\gamma_2\rangle = |S_y\rangle = \frac{1}{2i} \begin{bmatrix} 0 \\ -1 \\ 1 \\ 0 \end{bmatrix},$$

$$\langle\gamma_2| = 2\langle S_y| = [0 \quad -i \quad i \quad 0]. \quad (1.38)$$

Critical-Damping Modes Like the steady-state mode (1.36), the remaining two modes, $|\gamma_-\rangle = |\gamma_3\rangle$ and $|\gamma_+\rangle = |\gamma_4\rangle$, represent ensembles of atoms with spin polarization in the zx plane, perpendicular to the axis of rotation (the y axis) of the magnetic field. They can be written as

$$|\gamma_\pm\rangle = c_\pm |S_x\rangle + d_\pm |S_z\rangle = \frac{1}{2} \begin{bmatrix} d_\pm \\ c_\pm \\ c_\pm \\ -d_\pm \end{bmatrix}. \quad (1.39)$$

Using (1.39) with (1.28), we find that the eigenvalues are

$$\gamma_\pm = \gamma_c \pm \sqrt{\omega_c^2 - \omega^2}. \quad (1.40)$$

We can write the critical damping frequency and the critical damping rate γ_c as

$$\omega_c = (1/2 - f)\Gamma_p \quad \text{and} \quad \gamma_c = (1/2 + f)\Gamma_p + \Gamma_c, \quad (1.41)$$

and with the relative value of the coefficients given by

$$\begin{bmatrix} c_\pm \\ d_\pm \end{bmatrix} = \begin{bmatrix} \omega_c \pm \sqrt{\omega_c^2 - \omega^2} \\ \omega \end{bmatrix}. \quad (1.42)$$

The eigenvalues γ_\pm are real and distinct for $\omega^2 < \omega_c^2$, and they are complex-conjugate pairs if $\omega^2 > \omega_c^2$. At the critical damping frequency, when $\omega^2 = \omega_c^2$, the rates γ_+ and γ_- become identical, and from (1.42) we see that there is a single eigenvector for the degenerate damping rate γ_c .

Compactification If the transverse magnetic field is zero (if $\omega = 0$), the system has symmetry about the z axis and (1.11) reduces to

$$G = \Gamma_p A_p + \Gamma_c A_c$$

$$= \frac{1}{2} \begin{bmatrix} \Gamma_c & 0 & 0 & -4f\Gamma_p - \Gamma_c \\ 0 & 2\Gamma_p + 2\Gamma_c & 0 & 0 \\ 0 & 0 & 2\Gamma_p + 2\Gamma_c & 0 \\ -\Gamma_c & 0 & 0 & 4f\Gamma_p + \Gamma_c \end{bmatrix}. \quad (1.43)$$

From inspection of (1.10) and (1.43) we see that for zero transverse field, the population $\rho_{\alpha\alpha}$ couples only to the other population $\rho_{\beta\beta}$ and vice versa. The coherences $\rho_{\alpha\beta}$ and $\rho_{\beta\alpha}$ couple only to themselves. In such cases it is useful to partition the

Liouville space of the density matrix into “compactified” subspaces, that is, we drop elements of the density matrix that are guaranteed to have a negligible effect on other elements for some fundamental reason. Compactification can be done conveniently with logical variables. In the case described above, we will introduce the logical variable for populations

$$L = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \text{and} \quad |L\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \quad (1.44)$$

The definitions (1.15) for $|1^{\{S\}}\rangle$ and (1.16) for $|1^{\{S\}}\rangle$ appear to be identical to the definition (1.44) for L and $|L\rangle$, but in (1.15) and (1.16) the 1’s and 0’s represent real numbers, but in (1.44) 1 denotes the logical (Boolean) value true and 0 denotes the logical value false. A simple MATLAB statement to create the logical column vector L , representing $|L\rangle$, from the nonlogical column vector cPS , representing $|1^{\{S\}}\rangle$ and evaluated by Code 1.3 on page 8, is

Code 1.6

```
L=cPS>0;
```

In this example, populations are true and coherences are false. Slightly more complicated statements are needed to define a logical variable L that is true for coherences that are generated by magnetic resonance or modulated light, but is false for off-resonant coherences that are sure to be negligibly small.

Logical variables are a powerful tool to increase the efficiency of computer calculations. For example, if $crho$ is the computer variable denoting the column vector $|\rho\rangle$, then $crhoc=crho(L)$ is the shorter column vector representing the compactified density matrix of populations, for example,

$$\text{if } crho = \begin{bmatrix} 0.8 \\ 0.1 \\ 0.1 \\ 0.2 \end{bmatrix}, \quad \text{then } crhoc(L) = \begin{bmatrix} 0.8 \\ 0.2 \end{bmatrix}. \quad (1.45)$$

Logical variables can also be used to compactify the evolution matrix (1.43). For example, the MATLAB matrix G can be compactified to the matrix Gc with the statement, $Gc=G(L,L)$, for example,

$$\text{if } G = \begin{bmatrix} 0.05 & 0 & 0 & -0.85 \\ 0 & 1.1 & 0 & 0 \\ 0 & 0 & 1.1 & 0 \\ -0.05 & 0 & 0 & 0.85 \end{bmatrix}, \quad \text{then}$$

$$G(L,L) = \begin{bmatrix} 0.05 & -0.85 \\ -0.05 & 0.85 \end{bmatrix}. \quad (1.46)$$

As we shall show in subsequent examples, it is not necessary to define new compactified arrays like `crhoc` and `cG` above. One can simply enter statements like `chro(L)` and `G(L,L)` in lines of code where they are automatically interpreted as compactified quantities. Computer calculations are faster with the smaller, compactified vectors and matrices than with the original, often much larger ones. If the logical indices are chosen with good physical insight, there will be negligible loss of accuracy owing to the neglected terms.

Summary The hypothetical, spin-1/2 alkali-metal atom illustrates themes that we will discuss in more detail for the more complicated situations of real atoms. Some important points are:

- As illustrated in (1.3), the Liouville-space density matrix is conveniently represented as a column vector, $|\rho\rangle$, formed by placing each successive column of the Schrödinger-space density matrix, ρ , below the one to its left. In an analogous way, other Schrödinger-space operators like those of (1.16) can be transformed to column vectors.
- As indicated in (1.21), the expectation value $\langle X \rangle$ of a Schrödinger operator X is $\langle X \rangle = (X^\dagger|\rho\rangle$.
- The time evolution of the density matrix $|\rho\rangle$ is given by the first-order, matrix differential equation (1.10), $|\dot{\rho}\rangle = -G|\rho\rangle$.
- In simple cases – like the one we have discussed in this introduction – the evolution operator G of (1.10) is independent of time, t , or of ρ . For spin exchange between identical alkali-metal atoms, the damping operator G depends on ρ and (1.10) is nonlinear. When the atom is subjected to modulated magnetic fields or modulated light, G will be time-dependent. In these cases, it is often possible to define a “rotating coordinate system” where the evolution of the rotating-frame density matrix is given by an equation like (1.10), but with a time-independent G .
- As illustrated in (1.11) the damping operator G is a sum of terms representing various evolution mechanisms, for example, pumping, collisional relaxation, or spin interactions with external fields. Each process has a characteristic rate, such as the mean optical pumping rate Γ_p , the collisional rate Γ_c , or the rotation rate ω . The rate multiplies a dimensionless superoperator such as A_p , A_c , or S_y^{\odot} .
- The evolution operator G plays much the same role as the Hamiltonian operator H (or more precisely iH/\hbar) in Schrödinger space. There is no need for the operator G to be Hermitian or anti-Hermitian, and some of its eigenvalues may occur as complex-conjugate pairs. Unlike in Schrödinger space, for a given eigenvector γ_j of the evolution operator, G , the left eigenvectors $\langle\gamma_j|$ can differ from the Hermitian conjugate, $\langle\gamma_j| = |\gamma_j\rangle^\dagger$, of right eigenvectors $|\gamma_j\rangle$. In rare cases of critical damping, the eigenvectors, $|\gamma_j\rangle$, no longer form a complete basis for Liouville space, in contrast to Schrödinger space, where the Hermitian Hamiltonian, H , always has eigenvectors that form a complete basis.
- For relaxation and pumping processes that conserve atoms and keep the density matrix Hermitian, the damping operator G must satisfy the constraints

$(1^{\{S\}}|G = 0$ and $G = G^{\ddagger}$. These, and analogous identities that we will discuss later, are useful for validating computer-generated superoperators, which can have very large dimensions for real atoms, and which are not easy to check for coding errors.

- As illustrated by (1.45) and (1.46), one can omit elements of the density matrix that have a negligibly small effect on the physics for some fundamental reason. This compactification process is conveniently done with logical variables, and it can substantially speed up computer calculations with negligible loss of accuracy. For example, the Liouville space of ground-state ^{133}Cs atoms has 256 dimensions. If the experimental conditions are such that the coherence amplitudes are sure to be negligible, compactifying the full space to only the populations reduces the size of the Liouville space to only 16 dimensions. Adding in the two coherences for a “0–0” atomic clock transition still leaves a relatively small space of 18 dimensions.
- For very simple systems like the two-level atom discussed in this introduction, an analysis in Liouville space has no particular advantage over other methods. However, the systematic use of Liouville space is substantially more efficient than use of traditional methods for real atoms with many sublevels. This is partly because Liouville methods are better adapted to computer implementation of linear algebra, and partly because the computer codes are simpler to write and therefore less prone to errors. Coding statements often look almost the same as formal statements; for example, compare the line of code in Code 1.3 on page 8 that represents (1.31).

Units For the computer programs outlined in this book we will use cgs units, but we will use other units to enter data, for example megahertz for frequency or amagat for number density. A typical MATLAB program for real atoms will open with statements that set the values of fundamental physical constants, for example,

Code 1.7

```
clear;
kB=1.380e-16;%Boltzmann's constant in erg/K
NA=6.022e23;%Avogadro's number
c=2.9979e10;%speed of light in cm/s
muB=9.2741e-21;%Bohr magneton in erg/G
muN=5.051e-24;%nuclear magneton in erg/G
hP=6.6262e-27;%Planck's constant in erg/Hz
hbar=hP/(2*pi);%in erg s
re=2.816e-13;%classical electron radius in cm
amg=2.6868e19;%Loschmidt constant (amagat) in cm^{-3}
```
