Chapter 22
Time-Dependent Problems

The topics I will cover in the last three chapters of this book relate to time-dependent problems. Generally speaking, these will involve problems in which some classical, *time-dependent* interaction, such as that produced by an applied electric or magnetic field, induces transitions between states of a quantum system. I will first consider some very general features of time-dependent problems and then look in detail at a spin 1/2 system in a magnetic field and a two-level atom in an optical field. The density matrix of a single quantum system will be defined and the Bloch and optical Bloch equations will be derived. After studying these "exact" problems, I will look at approximation techniques involving time-dependent problems in Chap. 23, including both the sudden and adiabatic limits. Finally, I will discuss the transitions between a discrete state and a continuum of states in Chap. 24, including Fermi's golden rule.

22.1 Time-Dependent Problems

There are classes of problems in quantum mechanics in which an isolated quantum system interacts with some externally applied fields. The isolated quantum system is characterized by a Hamiltonian $\hat{H}_0$ and its interaction with the external fields by a time-dependent contribution $\hat{V}(t)$ to the total Hamiltonian $\hat{H}$. In Dirac notation the total Hamiltonian is written in matrix form as

$$\underline{\mathrm{H}}(t) = \underline{\mathrm{H}}_0 + \underline{\mathrm{V}}(t). \tag{22.1}$$

For example, $\underline{\mathrm{H}}_0$ can be the Hamiltonian associated with an isolated atom and $\underline{\mathrm{V}}(t)$ can represent the interaction energy of the atom with a classical optical field. If $\underline{\mathrm{H}}(t)$ depends on time, the energy is no longer a constant of the motion. Let the eigenkets of $\underline{\mathrm{H}}_0$ be denoted by $|n\rangle$, such that

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$$\underline{\mathrm{H}}_0|n\rangle = E_n|n\rangle, \tag{22.2}$$

where E_n is the eigenenergy associated with the eigenket $|n\rangle$.

Since the eigenkets are complete, I can expand the state vector as

$$|\psi(t)\rangle = \sum_n a_n(t)|n\rangle \tag{22.3}$$

and substitute this expansion into Schrödinger's equation,

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = [\underline{\mathrm{H}}_0 + \underline{\mathrm{V}}(t)]\,|\psi(t)\rangle, \tag{22.4}$$

to obtain the set of differential equations

$$i\hbar\sum_n \dot{a}_n(t)|n\rangle = \underline{\mathrm{H}}_0\sum_n a_n(t)|n\rangle + \underline{\mathrm{V}}(t)\sum_n a_n(t)|n\rangle. \tag{22.5}$$

Using the orthogonality of the eigenkets [that is, multiplying Eq. (22.5) by $\langle n'|$], I find that the state amplitudes evolve as

$$i\hbar\dot{a}_n(t) = E_n a_n(t) + \sum_n V_{nm}(t)a_n(t)\,, \tag{22.6}$$

where the matrix element $V_{nm}(t)$ is defined as

$$\begin{aligned} V_{nm}(t) &= \langle n|\hat{V}(t)|m\rangle \\ &= \int \psi_n^*(\mathbf{r})\hat{V}(t)\psi_m(\mathbf{r})d\mathbf{r}\,. \end{aligned} \tag{22.7}$$

I can write Eq. (22.6) as the matrix equation

$$i\hbar\dot{\mathbf{a}}(t) = \underline{\mathrm{E}}\mathbf{a}(t) + \underline{\mathrm{V}}(t)\mathbf{a}(t)\,, \tag{22.8}$$

in which $\mathbf{a}(t)$ is a vector [or, equivalently, a column matrix $\underline{\mathrm{a}}(t)$], $\underline{\mathrm{E}} = \underline{\mathrm{H}}_0$ is a diagonal matrix whose elements are the eigenvalues of $\hat{H}_0$ ($\underline{\mathrm{E}}$ is simply equal to $\underline{\mathrm{H}}_0$ written in the energy representation) and $\underline{\mathrm{V}}(t)$ is a matrix having elements $V_{nm}(t)$. The fact that $\underline{\mathrm{V}}(t)$ is not diagonal, in general, implies that there are *transitions* between the eigenstates of $\underline{\mathrm{H}}_0$.

To obtain the dynamics, I must solve Eq. (22.8) for the state amplitudes. If $\underline{\mathrm{V}}(t)$ is a finite matrix, the coupled equations can be solved numerically. As with any differential equation, you can obtain an *analytic* solution only if you already *know* the solution. You can guess a solution based upon what others have learned in the past. For example, based on the solution of the *scalar* equation

$$i\hbar\dot{x}(t) = f(t)x(t), \tag{22.9}$$

which is

$$x(t) = \exp\left[-\frac{i}{\hbar}\int_0^t f(t')dt'\right]x(0), \tag{22.10}$$

you might think (and you would have some company) that a solution to Eq. (22.8) is

$$\mathbf{a}(t) = \exp\left[-\frac{i}{\hbar}\left(\underline{\mathrm{E}}t + \int_0^t \underline{\mathrm{V}}(t')dt'\right)\right]\mathbf{a}(0), \tag{22.11}$$

but you would be wrong. That is, if you substitute the trial solution given by Eq. (22.11) into Eq. (22.8), it does not work if $\underline{\mathrm{V}}(t)$ and $\underline{\mathrm{V}}(t')$ do not commute. If $\underline{\mathrm{V}}$ is independent of time, you *can* write the solution as

$$\mathbf{a}(t) = \exp\left[-\frac{i}{\hbar}(\underline{\mathrm{E}} + \underline{\mathrm{V}})t\right]\mathbf{a}(0); \tag{22.12}$$

however, in general, it is impossible to obtain analytic solutions to Eq. (22.8) when $\underline{\mathrm{V}}$ is a function of time.

22.1.1 Interaction Representation

In some sense, I am done. Either I can solve Eq. (22.8) or I cannot. That does not prevent me from modifying the equation into what may be a more convenient form. Remember, however, that modifying the equation does not make it solvable, but it may reveal a structure where the solution is more apparent. The first such modification that I use, applicable to any time-dependent quantum problem, involves an *interaction representation*. The idea behind the interaction representation is to have the state amplitudes be *constant* in the absence of the interaction $\underline{\mathrm{V}}(t)$. To accomplish this, I must remove the rapidly varying phase factor $\exp(-iE_nt/\hbar)$ from the state amplitudes by writing

$$|\psi(t)\rangle = \sum_n c_n(t)\exp\left(-iE_nt/\hbar\right)|n\rangle. \tag{22.13}$$

It then follows from Schrödinger's equation that the amplitudes $c_n(t)$ of the interaction representation obey the differential equation

$$i\hbar\dot{c}_n(t) = \sum_m V_{nm}(t)c_m(t)\exp\left(i\omega_{nm}t\right) \equiv \sum_m V^I_{nm}(t)c_m(t), \tag{22.14}$$

where

$$\omega_{nm} = (E_n - E_m)/\hbar \tag{22.15}$$

is a transition frequency and

$$V^I_{nm}(t) = \exp(i\omega_{nm}t)\, V_{nm}(t) \tag{22.16}$$

is a matrix element in the interaction representation. Note that

$$c_n(t) = a_n(t) \exp(iE_n t/\hbar), \tag{22.17}$$

such that $|c_n(t)|^2 = |a_n(t)|^2$ is equal to the probability for the quantum system to be in state n.

In the interaction representation, the state vector can be written as

$$|\psi(t)\rangle = \sum_n c_n(t) \exp(-iE_n t/\hbar)\, |n\rangle \equiv \sum_n c_n(t) |n^I(t)\rangle, \tag{22.18}$$

where "eigenkets" $|n^I(t)\rangle = \exp(-iE_n t/\hbar)\, |n\rangle$ are time-dependent. It is important not to forget this time dependence when calculating expectation values of operators. In general, the interaction representation is used often in numerical solutions rather than the Schrödinger representation; in this manner, you need not start the integration until the interaction is turned on. In the Schrödinger representation, the phases of the state amplitudes evolve even in the absence of the interaction.

22.2 Spin 1/2 Quantum System in a Magnetic Field

As a first example, I consider the interaction of the spin 1/2 quantum system with an external magnetic field induction

$$\mathbf{B}(t) = B_0 \mathbf{u}_z + |B_x(t)| \cos[\omega t - \phi(t)]\, \mathbf{u}_x, \tag{22.19}$$

In other words, the z-component of the field is constant and the x-component is an oscillatory field having carrier frequency ω, amplitude $|B_x(t)|$, and phase $\phi(t)$. The interaction of a spin 1/2 quantum system with a magnetic field of the type given in Eq. (22.19) is not only of theoretical interest. For example, when a strong constant magnetic field is applied in the z-direction, and pulsed oscillating fields are applied in the x-direction that are in resonance with the transition between the spin states, it is possible to control the population difference between the spin up and spin down states, as well as the relative phase between the state amplitudes. The ability to control the dynamics of a spin 1/2 quantum system with a series of radio frequency pulses is the basis for *NMR* (nuclear magnetic resonance) and

MRI (magnetic resonance imaging). In MRI, the protons in hydrogen in the water molecule serve as the spin 1/2 quantum system.

For the sake of definiteness, I take the spin 1/2 quantum system to be an electron having $s = j = 1/2$ that is bound in the ground state of an atom having no hyperfine structure. The Hamiltonian characterizing the electron spin—magnetic field system is

$$\underline{\mathrm{H}}_B(t) = \beta_0 \boldsymbol{\sigma} \cdot \mathbf{B}(t), \tag{22.20}$$

where

$$\boldsymbol{\sigma} = \sigma_{\mathbf{x}} \mathbf{u}_x + \sigma_y \mathbf{u}_y + \sigma_z \mathbf{u}_z, \tag{22.21}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{22.22}$$

m_e is the electron mass, and $\beta_0 = e\hbar/2m_e$ is the Bohr magneton.

With $\mathbf{B}(t)$ given by Eq. (22.19), the Hamiltonian (22.20) can be written in terms of the Pauli matrices as

$$\underline{\mathrm{H}}_B(t) = \frac{\hbar}{2} \left\{ \omega_0 \sigma_z + 2\omega_x(t) \cos\left[\omega t - \phi(t)\right] \sigma_x \right\}, \tag{22.23}$$

where

$$\omega_0 = \frac{2\beta_0 B_0}{\hbar} = \frac{eB_0}{m_e} = 1.76 \times 10^{11}\, B_0(\mathrm{T})\ s^{-1} = 1.76 \times 10^7\, B_0(\mathrm{Gauss})\ s^{-1} \tag{22.24}$$

is the frequency spacing of the two spin states in the absence of the oscillating component of the field and

$$\omega_x(t) = \frac{\beta_0 \left| B_x(t) \right|}{\hbar}. \tag{22.25}$$

is a measure of the coupling field strength in frequency units. In frequency units, $\omega_0/2\pi = 28$ GHz/T$= 2.8$ MHz/Gauss. The physical system is represented schematically in Fig. 22.1a.

From Eqs. (22.6) and (22.23), it follows that the equation for the state amplitudes in the Schrödinger representation is

$$\dot{\mathbf{a}}_B(t) = -i \begin{pmatrix} \omega_0/2 & \omega_x(t) \cos[\omega t - \phi(t)] e^{i\omega_0 t} \\ \omega_x(t) \cos[\omega t - \phi(t)] e^{-i\omega_0 t} & -\omega_0/2 \end{pmatrix} \mathbf{a}_B(t), \tag{22.26}$$

with $\mathbf{a}_B = \left(a_\uparrow, a_\downarrow\right)$, and the up (down) arrow refers to the state having magnetic quantum number $1/2$ $(-1/2)$.

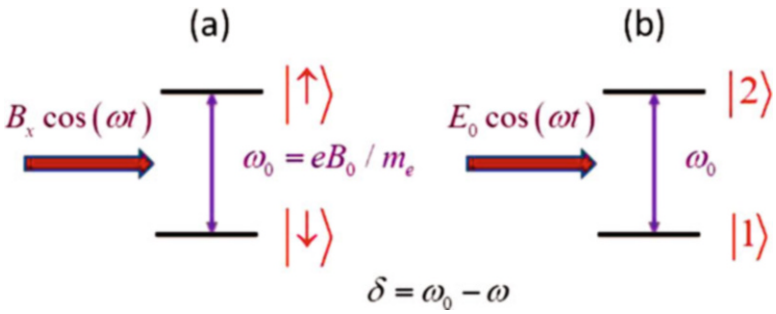

Fig. 22.1 Two-level quantum systems interacting with an external field. (**a**) A two-level spin system corresponding to an electron in an atom. An external magnetic field having a constant component B_0 in the z direction splits the spin up and spin down energy eigenkets, while an oscillating component $B_x \cos(\omega t)$ in the x direction drives transitions between the two spin states. (**b**) The analogous situation for a "two-level" atom in which an optical field [having electric field $E_0 \cos(\omega t)$] drives transitions between two electronic states. In both cases the two-level quantum system is assumed to be fixed at the origin. Generalizations to allow for time-dependent amplitudes and phases of the fields are included in the text

In general, these equations must be solved numerically (see problems). To get some insight into the nature of the response of the spin to the external magnetic field, I consider two cases where it is possible to get analytic solutions of the equations.

22.2.1 Analytic Solutions

22.2.1.1 $\omega_x(t) = \omega_x$ = Constant; $\omega = 0$; $\phi(t) = \phi$ = Constant

This limit corresponds to a constant field

$$\mathbf{B} = B_0 \mathbf{u}_z + B_x \mathbf{u}_x \,, \tag{22.27}$$

such that

$$\underline{\mathrm{H}}_B = \hbar \left(\frac{\omega_0 \sigma_z}{2} + \omega_x \cos\phi \, \sigma_x \right) = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & 2\omega_x \cos\phi \\ 2\omega_x \cos\phi & -\omega_0 \end{pmatrix} . \tag{22.28}$$

This Hamiltonian is representative of a generic two-level problem in which two levels are coupled by a *constant* interaction. The solution of Eq. (22.26) is

$$\begin{aligned} \mathbf{a}_B(t) &= \exp\left[-\frac{i}{2} \begin{pmatrix} \omega_0 & 2\omega_x \cos\phi \\ 2\omega_x \cos\phi & -\omega_0 \end{pmatrix} t \right] \mathbf{a}_B(0) \\ &= \exp\left[-i \left(\frac{\omega_0 \sigma_z}{2} + \omega_x \cos\phi \, \sigma_x \right) t \right] \mathbf{a}_B(0). \end{aligned} \tag{22.29}$$

The exponential is of the form

$$e^{-i\theta \mathbf{n}\cdot\boldsymbol{\sigma}} = \mathbf{1}\cos\theta - i\mathbf{n}\cdot\boldsymbol{\sigma}\sin\theta, \tag{22.30}$$

with

$$\mathbf{n} = \frac{2\omega_x \cos\phi \mathbf{u}_x + \omega_0 \mathbf{u}_z}{\sqrt{4\left(\omega_x \cos\phi\right)^2 + \omega_0^2}}; \quad \theta = \frac{\sqrt{4\left(\omega_x \cos\phi\right)^2 + \omega_0^2}}{2} t, \tag{22.31}$$

leading to the solution

$$a_\uparrow(t) = -i\frac{2\omega_x \cos\phi}{X} \sin\frac{Xt}{2} a_\downarrow(0) + \left[\cos\frac{Xt}{2} - i\frac{\omega_0}{X}\sin\frac{Xt}{2}\right] a_\uparrow(0)\,, \tag{22.32a}$$

$$a_\downarrow(t) = \left[\cos\frac{Xt}{2} + i\frac{\omega_0}{X}\sin\frac{Xt}{2}\right] a_\downarrow(0) - i\frac{2\omega_x \cos\phi}{X}\sin\frac{Xt}{2} a_\uparrow(0)\,, \tag{22.32b}$$

where

$$X = \sqrt{\omega_0^2 + 4\left(\omega_x \cos\phi\right)^2}. \tag{22.33}$$

If the initial condition is $a_\downarrow(0) = 1$, $a_\uparrow(0) = 0$, then

$$\left|a_\uparrow(t)\right|^2 = \frac{4\omega_x^2 \cos^2\phi}{\omega_0^2 + 4\omega_x^2 \cos^2\phi} \sin^2\left(Xt/2\right); \tag{22.34a}$$

$$\left|a_\downarrow(t)\right|^2 = \frac{\omega_0^2 + 4\omega_x^2 \cos^2\phi \cos^2\left(Xt/2\right)}{\omega_0^2 + 4\omega_x^2 \cos^2\phi}. \tag{22.34b}$$

Both upper and lower state populations oscillate as a function of time. These oscillations are referred to as *Rabi oscillations* (after I. I. Rabi). If $\omega_0 = 0$, the maximum value of the upper state population is equal to unity—in this limit, complete *inversion* of the population is possible whenever $\sin^2\left(Xt/2\right) = 1$.

22.2.1.2 $\omega_0 = 0$

If there is no longitudinal field [$B_z = 0$], the energy levels are degenerate and are coupled by the field oscillating in the x direction. Equations for the probability amplitudes obtained from Eq. (22.26) have the form

$$\dot{a}_\uparrow(t) = -if(t)a_\downarrow(t)\,; \tag{22.35a}$$

$$\dot{a}_\downarrow(t) = -if(t)a_\uparrow(t)\,, \tag{22.35b}$$

where

$$f(t) = \omega_x(t) \cos\left[\omega t - \phi(t)\right] . \tag{22.36}$$

By adding and subtracting the equations, I obtain

$$\dot{a}_\uparrow(t) \pm \dot{a}_\downarrow(t) = \mp i f(t) \left[a_\uparrow(t) \pm a_\downarrow(t)\right] , \tag{22.37}$$

for which the solution is

$$a_\downarrow(t) \pm a_\downarrow(t) = \left[a_\downarrow(0) \pm a_\downarrow(0)\right] e^{\mp i\theta(t)}, \tag{22.38}$$

where

$$\theta(t) = \int_0^t f(t')dt'. \tag{22.39}$$

Using this equation you can deduce easily that the state amplitudes evolve as

$$a_\uparrow(t) = \cos\left[\theta(t)\right] a_\uparrow(0) - i \sin\left[\theta(t)\right] a_\downarrow(0); \tag{22.40a}$$

$$a_\downarrow(t) = -i \sin\left[\theta(t)\right] a_\uparrow(0) + \cos\left[\theta(t)\right] a_\downarrow(0) , \tag{22.40b}$$

where

$$\theta(t) = \frac{1}{\hbar} \int_0^t V_{12}(t')dt' = \int_0^t \omega_x(t') \cos\left[\omega t' - \phi(t')\right] dt'. \tag{22.41}$$

Note that this solution is quite general; it remains valid for *any* degenerate, two-level quantum system whose degenerate energy levels are coupled by a time-dependent interaction having real matrix elements $V_{12}(t)$.

Although this is a simple solution, it can be used to illustrate some interesting physical concepts. If I take $\phi(t) = 0$ and $\omega_x(t) = \omega_x =$ constant, then

$$\theta(t) = \frac{\omega_x}{\omega} \sin \omega t, \tag{22.42}$$

which implies that the probability amplitudes contain *all* harmonics of the field. To see this more clearly I can expand $\cos\left[(\omega_x/\omega) \sin \omega t\right]$ in terms of a series of Bessel functions J_n using

$$\cos\left(z \sin\alpha\right) = J_0(z) + 2 \sum_{n=1}^{\infty} J_{2n}(z) \cos(2n\alpha) . \tag{22.43}$$

For example, if the initial state has $a_\downarrow(0) = 1$, $a_\uparrow(0) = 0$, then

$$\begin{aligned}\left|a_\uparrow(t)\right|^2 &= \sin^2\left(\frac{\omega_x}{\omega}\sin\omega t\right) = \frac{1-\cos\left(\frac{2\omega_x}{\omega}\sin\omega t\right)}{2} \\ &= \frac{1-J_0\left(\frac{2\omega_x}{\omega}\right)}{2} - \sum_{n=1}^{\infty} J_{2n}\left(\frac{2\omega_x}{\omega}\right)\cos(2n\omega t). \end{aligned} \tag{22.44}$$

In contrast to a harmonic oscillator, which is intrinsically a *linear* device, a two-level quantum system acts as a nonlinear device—the response does not depend linearly on the applied field and contains all harmonics of the driving field frequency. For $\omega_x/\omega \geq \pi/2$, there are still times for which complete inversion can occur, $\left|a_\uparrow(t)\right|^2 = 1$.

The time-averaged, spin-up population is

$$\overline{\left|a_\uparrow(t)\right|^2} = \frac{1-J_0\left(\frac{2\omega_x}{\omega}\right)}{2}. \tag{22.45}$$

The larger the applied frequency, the smaller is the time-averaged value of the spin-up state population, provided $\omega > 0.52\omega_x$. This is not surprising since the degenerate levels are resonant with a *static* field; the more rapid the oscillation of the field, the less effective it is in driving the transition. Interestingly, there are values of ω_x/ω for which $\overline{\left|a_\uparrow(t)\right|^2} > 1/2$. The maximum value of $\overline{\left|a_\uparrow(t)\right|^2} = 0.70$ occurs for $2\omega_x/\omega = 3.83$.

22.3 Two-Level Atom

The problem of a spin 1/2 particle in a magnetic field is isomorphic to the problem of a two-level atom interacting with an optical field. It is not difficult to imagine a situation where such a two-level approximation is valid. For example, if an optical field is nearly resonant with the ground to first excited state transition frequency of an atom whose ground and excited states have angular momentum quantum numbers $J = 0$ and $J = 1$, respectively, and if the field is z-polarized, then the field interacts effectively with only the ground state and the $m = 0$ sublevel of the excited state. To make matters simple, you can think of the atom as a one electron atom whose nucleus is located at position $\mathbf{R}$. The position of the electron relative to the nucleus is denoted by $\mathbf{r}$.

In dipole approximation, the interaction Hamiltonian is given by

$$\hat{V}(\mathbf{R},t) = \hat{V}_{AF}(\mathbf{R},t) \approx -\hat{\mathbf{p}}_e\cdot\mathbf{E}(\mathbf{R},t) = e\hat{\mathbf{r}}\cdot\mathbf{E}(\mathbf{R},t)\,, \tag{22.46}$$

where $\hat{\mathbf{p}}_e = -e\hat{\mathbf{r}}$ is the atomic dipole moment operator (a matrix in the Dirac picture) and $\mathbf{E}(\mathbf{R}, t)$ is the applied electric field, evaluated at the nuclear position. Recall that the charge of the electron is $-e$ in my notation. If atomic motion is neglected as I assume, I can set $\mathbf{R} = \mathbf{0}$.

The applied electric field at the nucleus of the atom is assumed to vary as

$$\mathbf{E}(t) = \mathbf{u}_z \, |E_0(t)| \cos\left[\omega t - \varphi(t)\right] = \frac{1}{2}\mathbf{u}_z |E_0(t)| \left[e^{i\varphi(t)}e^{-i\omega t} + e^{-i\varphi(t)}e^{i\omega t}\right], \tag{22.47}$$

where

$$\frac{1}{2}E_0(t)e^{-i\omega t} = \frac{1}{2}\,|E_0(t)|\, e^{i\varphi(t)}e^{-i\omega t} \tag{22.48}$$

is the *positive frequency component* of the field,

$$E_0(t) = |E_0(t)|\, e^{i\varphi(t)} \tag{22.49}$$

is the complex field amplitude, ω is the carrier frequency of the field, $|E_0(t)|$ is the field amplitude, and $\varphi(t)$ is the field phase. Both the amplitude and phase can be functions of time. A time-varying amplitude could correspond to a pulse envelope, while a time-varying phase gives rise to a frequency "chirp" (a frequency that varies in time). With this choice of field, the interaction Hamiltonian becomes

$$\hat{V}(t) = e\hat{z}|E_0(t)| \cos\left[\omega t - \varphi(t)\right] \,, \tag{22.50}$$

where $\hat{z}$ is the z-component of the position operator.

For the two-level atom, I take the energy of the ground state as $-\hbar\omega_0/2$ and that of the excited state as $\hbar\omega_0/2$. Denoting the ground state eigenket as $|1\rangle$ and the excited state eigenket by $|2\rangle$, I write the probability amplitudes as

$$\mathbf{a}(t) = \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} \tag{22.51}$$

and matrix elements of the interaction Hamiltonian as

$$V_{12}(t) = ez_{12}\,|E_0(t)| \cos\left[\omega t - \varphi(t)\right]; \tag{22.52a}$$

$$V_{21}(t) = ez_{21}\,|E_0(t)| \cos\left[\omega t - \varphi(t)\right] \,; \tag{22.52b}$$

$$V_{11} = V_{22} = 0\,, \tag{22.52c}$$

where

$$z_{12} = \langle 1|\hat{z}|2\rangle = \langle 2|\hat{z}|1\rangle^* = z_{21}^* \,. \tag{22.53}$$

The diagonal elements of the interaction Hamiltonian vanish since the operator $\hat{z}$ has odd parity. In general the matrix element z_{12} is complex, but any *single* transition matrix element can be taken as real by an appropriate choice of phase in the wave function (however, if z_{12} is taken to be real, then one is not at liberty to take x_{12} real since the phase of the electronic part of the wave function has been fixed—the matrix element of *one* component only of $\mathbf{r}_{12}$ can be taken as real and this choice determines whether or not the other components are real or complex). Therefore I set

$$ez_{12} = ez_{21} = -(p_{ez})_{12} \ \text{(real)}\,, \tag{22.54}$$

$$V_{12}(t) = V_{21}(t) = -(p_{ez})_{12}|E_0(t)|\cos\left[\omega t - \phi(t)\right]\,, \tag{22.55}$$

and write the Hamiltonian as

$$\underline{\mathrm{H}}(t) = \underline{\mathrm{H}}_0 + \underline{\mathrm{V}}(t) = \frac{\hbar}{2}\begin{pmatrix} -\omega_0 & 0 \\ 0 & \omega_0 \end{pmatrix} + \hbar\begin{pmatrix} 0 & |\Omega_0(t)|\cos\left[\omega t - \phi(t)\right] \\ |\Omega_0(t)|\cos\left[\omega t - \phi(t)\right] & 0 \end{pmatrix}\,, \tag{22.56}$$

where

$$\Omega_0(t) = \frac{-(p_{ez})_{12}E_0(t)}{\hbar} = \frac{ez_{12}E_0(t)}{\hbar} = |\Omega_0(t)|\,e^{i\varphi(t)} \tag{22.57}$$

is referred to as the *Rabi frequency* and is a measure of the atom–field interaction strength in frequency units. The Rabi frequency is defined such that it is positive for positive $E_0(t)$ and z_{12}. For the Hamiltonian given in Eq. (22.56), Eq. (22.8) for the probability amplitudes $\mathbf{a}(t)$ can be written as

$$\dot{\mathbf{a}}(t) = -\frac{i}{2}\begin{pmatrix} -\omega_0 & 2\,|\Omega_0(t)|\cos\left[\omega t - \phi(t)\right] \\ 2\,|\Omega_0(t)|\cos\left[\omega t - \phi(t)\right] & \omega_0 \end{pmatrix}\mathbf{a}(t)\,. \tag{22.58}$$

This equation can be solved numerically.

The Hamiltonian given in Eq. (22.56) can be recast as

$$\underline{\mathrm{H}}(t) = -\frac{\hbar\omega_0}{2}\sigma_z + \hbar\,|\Omega_0(t)|\cos\left[\omega t - \phi(t)\right]\sigma_x\,. \tag{22.59}$$

This is the same type of Hamiltonian that we encountered for the interaction of the electron spin with a magnetic-field. The sign of the lead terms in the Hamiltonians (22.59) and (22.23) differ, however, since, for the optical case, I have chosen the basis $\mathbf{a} = (a_1, a_2)$, while, for the magnetic case, the standard convention for the Pauli matrices requires that I take $\mathbf{a}_B = \left(a_\uparrow, a_\downarrow\right)$. The connection between the two cases is given by the substitutions:

$$(a_1, a_2) \Leftrightarrow \left(a_\downarrow, a_\uparrow\right); \tag{22.60a}$$

$$\omega_0 \Leftrightarrow \frac{2\beta_0 B_0}{\hbar}; \tag{22.60b}$$

$$|\Omega_0(t)| \cos\left[\omega t - \phi(t)\right] \Leftrightarrow \omega_x(t) \cos\left[\omega t - \phi(t)\right]. \tag{22.60c}$$

Although the equations for the two-level atom interacting with an electric field and the spin system interacting with a magnetic field look the same, the physical values of the parameters for the two systems differ markedly. That is, the frequency separation of the spin up and spin down states in a constant external magnetic field can range between 0 Hz and 10 GHz, while radio-frequency (rf) coupling strengths $\omega_x(t)$ are typically less than 1.0 MHz. In the optical case, electronic transition frequencies ω_0 are of order 10^{14}–10^{16} Hz and coupling strengths vary, but are typically much less than the frequency separation of the levels. Only for intense laser pulses having intensities greater than 10^{17} W/cm^2 can the coupling strength be comparable to the optical frequency separations. For a typical cw (continuous-wave) lasers having a few mW of power, coupling strengths are typically in the MHz to GHz range. Given this qualitative difference in the magnetic and electric cases, it is not surprising that different approximation schemes are used in the two cases. You will see that a *rotating wave approximation* is usually a good approximation for atom–optical field interactions, based on the assumption that $\omega_0 \gg |\Omega_0(t)|$, but this is not necessarily so for the magnetic case.

I will restrict the discussion to the optical case, but you should appreciate the fact that the discussion applies equally well to the magnetic field case if $|\omega_x(t)| \ll \omega_0$ and $|\omega - \omega_0| \,/\, |\omega + \omega_0| \ll 1$, conditions under which many NMR experiments are carried out.

22.3.1 Rotating-Wave or Resonance Approximation

Although Eq. (22.58) can be solved numerically, it is best to gain some physical insight into this equation before launching into any solutions. You shouldn't be deceived by the apparent simplicity of these coupled equations. There are books devoted to these equations and even numerical solutions can be difficult to obtain in certain limits.

Without solving the problem, you can ask under what conditions the field is effective in driving transitions between levels 1 and 2. I assume that the amplitude $|\Omega_0(t)|$ and phase $\phi(t)$ of the field are slowly varying on a time scale of order ω^{-1}. In this limit, the field can be considered to be *quasi-monochromatic*. Moreover, I assume that $|(\omega_0 - \omega)\,/(\omega_0 + \omega)| \ll 1$ and $|\Omega_0(t)/(\omega_0 + \omega)| \ll 1$. Under these assumptions, the field is effective in driving the 1-2 transition provided $|\omega_0 - \omega|$ is small compared with $|\Omega_0(t)|$.

The equation for $\dot{\mathbf{a}}(t)$ can be written as

$$\dot{\mathbf{a}}(t) = -\frac{i}{2}\begin{pmatrix} -\omega_0 & \Omega_0(t)e^{-i\omega t} + \Omega_0^*(t)e^{i\omega t} \\ \Omega_0(t)e^{-i\omega t} + \Omega_0^*(t)e^{i\omega t} & \omega_0 \end{pmatrix}\mathbf{a}(t)\,. \tag{22.61}$$

In the interaction representation, the corresponding equation for $\dot{\mathbf{c}}(t)$ is

$$\dot{\mathbf{c}}(t) = -\frac{i}{2}\begin{pmatrix} 0 & \Omega_0(t)e^{-i(\omega_0+\omega)t} + \Omega_0^*(t)e^{-i\delta t} \\ \Omega_0(t)e^{i\delta t} + \Omega_0^*(t)e^{i(\omega_0+\omega)t} & 0 \end{pmatrix}\mathbf{c}(t)\,, \tag{22.62}$$

where

$$\mathbf{c}(t) = \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \tag{22.63}$$

and

$$\delta = \omega_0 - \omega \tag{22.64}$$

is the *atom-field detuning*.

In the interaction representation we see that there are terms that oscillate with frequency $\omega_0 + \omega$ and those that oscillate at frequency δ. Moreover there can also be oscillation at frequency $|\Omega_0(t)|$. As long as $|\Omega_0(t)/(\omega_0+\omega)| \ll 1, |\delta/(\omega_0+\omega)| \ll 1$, as is assumed, the rapidly oscillating terms do not contribute much since they average to zero in a very short time. In other words, if I take a *coarse-grain time average* over a time interval much greater than $1/(\omega_0+\omega)$, the contribution from these rapidly varying terms is negligibly small compared with the slowly varying terms. The neglect of such terms is called the *rotating-wave approximation* (RWA) or *resonance approximation*. The reason for the nomenclature "rotating-wave" will soon become apparent. In the RWA, Eqs. (22.61) and (22.62) reduce to

$$\dot{\mathbf{a}}(t) = -\frac{i}{2}\begin{pmatrix} -\omega_0 & \Omega_0^*(t)e^{i\omega t} \\ \Omega_0(t)e^{-i\omega t} & \omega_0 \end{pmatrix}\mathbf{a}(t)\,; \tag{22.65}$$

$$\dot{\mathbf{c}}(t) = -\frac{i}{2}\begin{pmatrix} 0 & \Omega_0^*(t)e^{-i\delta t} \\ \Omega_0(t)e^{i\delta t} & 0 \end{pmatrix}\mathbf{c}(t)\,. \tag{22.66}$$

In component form, Eq. (22.66) is

$$\dot{c}_1(t) = -i\chi^*(t)e^{-i\delta t}c_2(t) \tag{22.67a}$$

$$\dot{c}_2(t) = -i\chi(t)e^{i\delta t}c_1(t)\,. \tag{22.67b}$$

where

$$\chi(t) = \Omega_0(t)/2, \tag{22.68}$$

Equations (22.67) also look deceptively simple. For a wide range of parameters, they are easy to solve numerically; however, if the envelope $\chi(t)$ corresponds to a pulse having duration T and if $|\delta|\,T \gg 1$, the numerical solutions can become extremely challenging. The reason for this is that the transition amplitudes are exponentially small in $|\delta|\,T$ requiring very small round-off errors, while the step size required for the calculations varies inversely with $|\delta|\,T$. The effective two-level atom-optical field system is depicted schematically in Fig. 22.1b. To gain some insight into the atom-field dynamics, I look at some limits in which an analytic solution of Eqs. (22.67) can be obtained.

22.3.2 Analytic Solutions

When

$$\chi(t) = |\chi(t)|e^{i\phi(t)} \tag{22.69}$$

is a function of time, there are very few analytic solutions of Eqs. (22.67), although there are certain combinations of $|\chi(t)|$ and $\phi(t)$ for which such solutions can be found. If $\phi(t)$ is constant and $\delta \neq 0$ the only smooth symmetric pulse shape for which an analytic solution is possible is the hyperbolic secant pulse shape.[1] In that case the amplitudes can be expressed as hypergeometric functions. Analytic solutions are also possible for [$\chi(t)$ real] and $\delta = 0$, or for $\chi(t) =$ constant, limiting cases that I now consider.

22.3.2.1 $\chi(t)$ real, $\delta = 0$

In this case, the amplitude equations (22.67) become

$$\dot{c}_1(t) = -i\chi(t)c_2(t); \tag{22.70a}$$

$$\dot{c}_2(t) = -i\chi(t)c_1(t). \tag{22.70b}$$

These equations have the same form as Eqs. (22.35), so the solution is

$$c_1(t) = \cos[\theta(t)]\,c_1(0) - i\sin[\theta(t)]\,c_2(0); \tag{22.71a}$$

$$c_2(t) = -i\sin[\theta(t)]\,c_1(0) + \cos[\theta(t)]\,c_2(0)\,, \tag{22.71b}$$

where

$$\theta(t) = \int_0^t \chi(t')dt'. \tag{22.72}$$

[1] N. Rosen and C. Zener, *Double Stern-Gerlach experiment and related collision phenomena*, Physical review **40**, 502–507 (1932).

In the case of an applied field pulse which "turns on" at $t = -\infty$, the initial conditions should be taken at $t = -\infty$, in which case Eqs. (22.71) are replaced by

$$c_1(t) = \cos[\theta(t)]\, c_1(-\infty) - i \sin[\theta(t)]\, c_2(-\infty) \tag{22.73a}$$

$$c_2(t) = -i \sin[\theta(t)]\, c_1(-\infty) + \cos[\theta(t)]\, c_2(-\infty)\,, \tag{22.73b}$$

with

$$\theta(t) = \int_{-\infty}^{t} \chi(t')dt'. \tag{22.74}$$

Note that, if at $t = -\infty$, $c_1(-\infty) = 1$ and $c_2(-\infty) = 0$, then

$$|c_2(\infty)|^2 = \sin^2(A/2)\,, \tag{22.75}$$

where

$$A \equiv 2\theta(\infty) = \int_{-\infty}^{\infty} \Omega_0(t')dt' = 2\int_{-\infty}^{\infty} \chi(t')dt' \tag{22.76}$$

is referred to as the *pulse area*. The pulse area determines how much population is transferred from the initial to final state. For reasons to be discussed in connection with the Bloch vector, A is defined such that a pulse area of π corresponds to a complete inversion, $|c_1(\infty)| = 0$, $|c_2(\infty)| = 1$, while $A = \pi/2$, results in an equal superposition of ground and excited states, $|c_1(\infty)| = |c_2(\infty)| = 1/\sqrt{2}$.

I have arrived at a pretty interesting result. You can control the degree of excitation that is achieved by a proper choice of pulse area, I might note, however, that the use of a π pulse for level inversion is not a "robust" method (when I was young, "robust" was used only to describe coffee). One must insure that the pulse intensity is uniform over the entire sample and that the pulse area is exactly equal to π to insure that all the atoms are inverted. There are other methods for achieving level inversion that are more robust. One such method is discussed in the next chapter.

22.3.2.2 $\chi(t) = \Omega_0/2 =$ Constant

In this case, Eqs. (22.67) reduce to

$$\dot{c}_1(t) = -\frac{i}{2}\Omega_0^* e^{-i\delta t} c_2(t); \tag{22.77a}$$

$$\dot{c}_2(t) = -\frac{i}{2}\Omega_0 e^{i\delta t} c_1(t)\,. \tag{22.77b}$$

Taking the derivative of Eq. (22.77b) and using Eq. (22.77a), I obtain

$$\ddot{c}_2(t) - i\delta\dot{c}_2(t) + \frac{|\Omega_0|^2}{4}c_2(t) = 0. \tag{22.78}$$

The solution of Eq. (22.78) is

$$c_2(t) = e^{i\delta t/2}\left[A\cos\left(\frac{\Omega t}{2}\right) + B\sin\left(\frac{\Omega t}{2}\right)\right]. \tag{22.79}$$

where

$$\Omega = \sqrt{\delta^2 + |\Omega_0|^2} \tag{22.80}$$

is known as the *generalized Rabi frequency*. In a similar manner you can obtain the solution

$$c_1(t) = e^{-i\delta t/2}\left[D\cos\left(\frac{\Omega t}{2}\right) + E\sin\left(\frac{\Omega t}{2}\right)\right]. \tag{22.81}$$

Only two of the integration constants A, B, D, E can be independent since I started with two, first order coupled differential equations—the constants are related through the differential equations. It is convenient to take A and D as independent since, clearly, $A = c_2(0)$ and $D = c_1(0)$. Using Eqs. (22.77), (22.78) and (22.79), you can then show that

$$E = i\frac{\delta}{\Omega}c_1(0) - i\frac{\Omega_0^*}{\Omega}c_2(0) \tag{22.82}$$

and

$$B = -i\frac{\Omega_0}{\Omega}c_1(0) - i\frac{\delta}{\Omega}c_2(0)\,. \tag{22.83}$$

Finally, the solution of Eqs. (22.77) is

$$c_1(t) = e^{-i\delta t/2}\left\{\begin{array}{c}\left[\cos\left(\frac{\Omega t}{2}\right) + i\frac{\delta}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\right]c_1(0)\\ -i\frac{\Omega_0^*}{\Omega}\sin\left(\frac{\Omega t}{2}\right)c_2(0)\end{array}\right\}\;; \tag{22.84a}$$

$$c_2(t) = e^{i\delta t/2}\left\{\begin{array}{c}-i\frac{\Omega_0}{\Omega}\sin\left(\frac{\Omega t}{2}\right)c_1(0)\\ +\left[\cos\left(\frac{\Omega t}{2}\right) - i\frac{\delta}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\right]c_2(0)\end{array}\right\}. \tag{22.84b}$$

This solution is of *fundamental* importance since it gives the response of a two-level atom to a monochromatic field. Note that the amplitudes depend *nonlinearly* on the applied amplitude—an atom acts as a nonlinear device, in contrast to an harmonic oscillator.

If $c_1(0) = 1; c_2(0) = 0$, then

$$|c_2(t)|^2 = \frac{|\Omega_0|^2}{\Omega^2} \sin^2\left(\frac{\Omega}{2}t\right) = \frac{|\Omega_0|^2}{\delta^2 + |\Omega_0|^2} \sin^2\left(\frac{\sqrt{\delta^2 + |\Omega_0|^2}}{2}t\right). \tag{22.85}$$

The population undergoes Rabi oscillations or *Rabi flopping* as a function of time. The time-averaged excited state population is

$$\overline{|c_2(t)|^2} = \frac{1}{2}\frac{|\Omega_0|^2}{\Omega^2} = \frac{1}{2}\frac{|\Omega_0|^2}{\delta^2 + |\Omega_0|^2}. \tag{22.86}$$

For $|\delta| \gg |\Omega_0|$, $\overline{|c_2(t)|^2} \approx |\Omega_0|^2/(2\delta^2)$. This is a somewhat surprising result. Even though the field is off resonance, the time-averaged transition probability falls off inversely only as $1/\delta^2$. In fact, I can turn off the field at a time $t = T = \pi/\Omega$ and find that $|c_2(T)|^2 \approx |\Omega_0|^2/\delta^2$. From the energy-time "uncertainty principle," you might expect that the transition probability would vanish at least *exponentially* with $|\delta| T$ (recall that increasing the light intensity in the photoelectric experiment does not increase the number of photoelectrons if the field frequency is not sufficiently high). What is going on?

Had the field been turned on and off *smoothly*, one would indeed find that $|c_2(t)|^2 \sim e^{-f(|\delta|T)}$, where f is some positive function. However, in the calculation that was carried out, the field is turned on *instantaneously* at $t = 0$ and turned off *instantaneously* at $t = T$. Owing to the point jump discontinuities, the Fourier components of a step function vary inversely with δT, rather than as an exponentially decaying function of $|\delta| T$.

22.3.3 Field-Interaction Representation

There is another representation that is especially useful when a single quasi-monochromatic field drives transitions between two levels or two manifolds of levels. Instead of extracting the atomic frequency, I can extract the *laser* frequency (and phase) and write

$$\begin{aligned} |\psi(t)\rangle &= \tilde{c}_1(t)e^{i[\omega t/2 - \phi(t)/2]}|1\rangle + \tilde{c}_2(t)e^{-i[\omega t/2 - \phi(t)/2]}|2\rangle \\ &\equiv \tilde{c}_1(t)|\tilde{1}(t)\rangle + \tilde{c}_2(t)|\tilde{2}(t)\rangle, \end{aligned} \tag{22.87}$$

where

$$|\tilde{1}(t)\rangle = e^{i[\omega t/2 - \phi(t)/2]}|1\rangle; \tag{22.88a}$$

$$|\tilde{2}(t)\rangle = e^{-i[\omega t/2 - \phi(t)/2]}|2\rangle \tag{22.88b}$$

are time-dependent kets, as were the standard interaction representation kets. The transformation from the Schrödinger representation to this *field interaction representation* can be written as

$$a_1(t) = \tilde{c}_1(t)e^{i[\omega t/2-\phi(t)/2]}; \tag{22.89a}$$

$$a_2(t) = \tilde{c}_2(t)e^{-i[\omega t/2-\phi(t)/2]}, \tag{22.89b}$$

and from the interaction representation to the field interaction as

$$c_1(t) = \tilde{c}_1(t)e^{-i[\delta t/2+\phi(t)/2]}; \tag{22.90a}$$

$$c_2(t) = \tilde{c}_2(t)e^{i[\delta t/2+\phi(t)/2]}. \tag{22.90b}$$

Note that

$$\left|a_j(t)\right|^2 = \left|c_j(t)\right|^2 = \left|\tilde{c}_j(t)\right|^2;$$

state population probabilities are the same in all representations. It follows from Eqs. (22.90) and (22.62) that

$$\dot{\tilde{c}}_1(t) = i\frac{\delta(t)}{2}\tilde{c}_1(t) - i\frac{|\Omega_0(t)|}{2}\tilde{c}_2(t) - i\frac{|\Omega_0(t)|}{2}e^{-2i[\omega t-\phi(t)]}\tilde{c}_2(t); \tag{22.91a}$$

$$\dot{\tilde{c}}_2(t) = -i\frac{\delta(t)}{2}\tilde{c}_2(t) - i\frac{|\Omega_0(t)|}{2}\tilde{c}_1(t) - i\frac{|\Omega_0(t)|}{2}e^{2i[\omega t-\phi(t)]}\tilde{c}_1(t)\,, \tag{22.91b}$$

where

$$\delta(t) = \delta + \dot{\phi}(t) = \omega_0 - \left[\omega - \dot{\phi}(t)\right] \tag{22.92}$$

and $\left[\omega - \dot{\phi}(t)\right]$ can be viewed as the time-varying frequency of the optical field. In a frame rotating at the field frequency, there are rapidly varying terms oscillating at twice the field frequency. The neglect of such terms in this rotating frame is the origin of the nomenclature RWA. In the RWA, the equations reduce to

$$\dot{\tilde{c}}_1(t) = i\frac{\delta(t)}{2}\tilde{c}_1(t) - i\frac{|\Omega_0(t)|}{2}\tilde{c}_2(t)\,; \tag{22.93a}$$

$$\dot{\tilde{c}}_2(t) = -i\frac{\delta(t)}{2}\tilde{c}_2(t) - i\frac{|\Omega_0(t)|}{2}\tilde{c}_1(t)\,, \tag{22.93b}$$

or

$$i\hbar\dot{\tilde{\mathbf{c}}} = \widetilde{\underline{\mathrm{H}}}(t)\tilde{\mathbf{c}}(t)\,, \tag{22.94}$$

where

$$\underline{\widetilde{\mathrm{H}}}(t) = \frac{\hbar}{2}\begin{pmatrix} -\delta(t) & |\Omega_0(t)| \\ |\Omega_0(t)| & \delta(t) \end{pmatrix}. \tag{22.95}$$

In terms of the Pauli matrices, the RWA Hamiltonian is

$$\underline{\widetilde{\mathrm{H}}}(t) = \frac{\hbar}{2}\left[-\delta(t)\sigma_z + |\Omega_0(t)|\,\sigma_x\right]. \tag{22.96}$$

The effective energy levels in the field interaction representation are $\mp\hbar\delta(t)/2$ and the magnitude of the Rabi frequency determines the coupling of the levels. Remember that the *eigenkets* of $\underline{\widetilde{\mathrm{H}}}(t)$ are time-dependent [even if $\Omega_0(t)$ is constant].

You might ask which representation is the best to use. The answer is, "It depends." Rarely does one use the Schrödinger representation, except in formal manipulations of the equations. For the two-level problem and arbitrary $\Omega_0(t)$, there is not much difference between the interaction and field interaction representations. Differences between the two representations arise in problems involving more than two levels and more than a single field. Generally speaking, the field interaction representation is most useful when a single field drives transitions between two manifolds of levels, while the interaction representation should be used when fields having two or more frequencies drive transitions between two levels or two manifolds of levels.

22.4 Density Matrix for a Single Atom

In the previous section, I showed in detail how to obtain solutions of the time-dependent Schrödinger equation for the state amplitudes of a two-level spin system interacting with a magnetic field and a two-level atom interacting with an optical field. To make connection with experiment, however, you need to know how the state amplitudes are related to the possible outcomes of measurements. Any physical measurement yields real results, while the state amplitudes are complex. From the considerations of Chap. 5, you know that the expectation value of any Hermitian operator corresponding to a physical observable depends on bilinear products of the state amplitudes. For example, if you were to calculate the expectation value of the electric dipole moment of a two-level atom, you would find that it depends on the bilinear products $a_1^*(t)a_2(t)$ and $a_2^*(t)a_1(t)$ since

$$\begin{aligned} \langle\hat{\mathbf{r}}\rangle &= \langle\psi(t)|\hat{\mathbf{r}}|\psi(t)\rangle \\ &= \langle a_1(t)\psi_1 + a_2(t)\psi_2|\hat{\mathbf{r}}|a_1(t)\psi_1 + a_2(t)\psi_2\rangle \\ &= a_1^*(t)a_2(t)\langle 1|\hat{\mathbf{r}}|2\rangle + \text{c.c.}, \end{aligned} \tag{22.97}$$

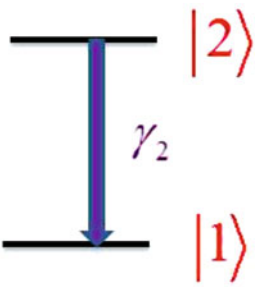

Fig. 22.2 Spontaneous emission in a two-level atom

where the fact that $\hat{\mathbf{r}}$ is an odd parity operator has been used.

A knowledge of the state amplitudes allows you to calculate the expectation values of any operators. Although all the information is contained in the state amplitudes, we are not necessarily interested in *all* the information. If we measure only *part* of the information content of a system, an amplitude approach is often no longer satisfactory. This concept can be illustrated with a simple example.

Let us look at spontaneous decay in a two-level atom, Fig. 22.2. As a result of spontaneous decay (to be discussed in Chap. 24), the upper state population $n_2(t) = |a_2(t)|^2$ decreases and the lower state population $n_1(t) = |a_1(t)|^2$ increases according to

$$\dot{n}_2(t) = -\gamma_2 n_2(t); \tag{22.98a}$$

$$\dot{n}_1(t) = \gamma_2 n_2(t)\,, \tag{22.98b}$$

where the excited state decay rate γ_2 is real. Is it possible to account for this decay in an amplitude picture? You can try the equation

$$\dot{a}_2(t) = -\frac{\gamma_2}{2} a_2(t)\,, \tag{22.99}$$

which implies

$$\frac{d}{dt}|a_2(t)|^2 = \frac{d}{dt}[a_2(t)a_2^*(t)] = \dot{a}_2(t)a_2^*(t) + a_2(t)\dot{a}_2^*(t) = -\gamma_2|a_2(t)|^2\,. \tag{22.100}$$

It works! But try to reproduce Eq. (22.98b) in a simple amplitude picture—you will find it impossible to do so.

In problems of this nature, where atoms interact with a thermal bath, such as the vacuum field for spontaneous emission, the total Hamiltonian consists of a term for the atoms, a term for the fields and a term for the atom–field interaction. The vacuum field is quantized, so all terms in the Hamiltonian are time-independent. The state amplitudes are labeled by the eigenvalues associated with *both* the atoms

and the fields. If we are interested in the atomic state variables only, it is necessary to average over the field variables. A convenient method for carrying out this average involves the *density matrix* of the atom-field system. In statistical mechanics, the density matrix is used to characterize an ensemble of atoms. Even when considering a *single* atom interacting with external fields, the density matrix approach is useful—so let me start there.

The expectation value of an arbitrary Hermitian operator $\hat{A}$ in the state

$$|\psi(t)\rangle = \sum_n a_n(t)|n\rangle \tag{22.101}$$

of a single atom (possibly interacting with time-dependent external fields, but *not* with a thermal bath) is given by

$$\begin{aligned}\langle\psi(t)|\hat{A}|\psi(t)\rangle &= \sum_{n,m}\langle m|a_m^*(t)\hat{A}a_n(t)|n\rangle = \sum_{n,m} a_m^*(t)a_n(t)\langle m|\hat{A}|n\rangle \\ &= \sum_{n,m} a_m^*(t)a_n(t)A_{mn}\,,\end{aligned} \tag{22.102}$$

where the $a_n(t)$ are the atomic state amplitudes. I want to define a matrix $\underline{\rho}(t)$ whose elements in the energy basis are equal to $a_n(t)a_m^*(t)$. A matrix satisfying this criterion is the *density matrix*

$$\underline{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|\,, \tag{22.103}$$

since

$$\langle n|\underline{\rho}(t)|m\rangle = \langle n|\psi(t)\rangle\langle\psi(t)|m\rangle = \sum_{p,p'} a_p(t)a_{p'}^*(t)\,\langle n\,|p\rangle\,\langle p'\,|m\rangle = a_n(t)a_m^*(t)\,. \tag{22.104}$$

Note that $\underline{\rho}(t)$ is *not* a bona fide Schrödinger operator since it is time-dependent, whereas all operators in the Schrödinger picture are taken as time independent. With this definition

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \sum_{n,m}\rho_{nm}(t)A_{mn} = \mathrm{Tr}\left(\underline{\rho}(t)\underline{\mathrm{A}}\right)\,. \tag{22.105}$$

where Tr stands for "trace."

In the energy basis

$$\underline{\rho}(t) = \sum_{n,m}\rho_{nm}(t)|n\rangle\langle m|\,; \tag{22.106}$$

recall that $|n\rangle\langle m|$ is a matrix with a 1 in the nm location and zeroes elsewhere. It is also possible to expand $\underline{\rho}(t)$ in other bases, such as an irreducible tensor basis. It is easy to establish some properties for $\underline{\rho}(t)$ for the single atom case. First, I note that

$$\underline{\rho}(t) = \underline{\mathrm{a}}(t)\underline{\mathrm{a}}^{\dagger}(t)\,, \tag{22.107}$$

where $\underline{\mathrm{a}}$ is interpreted as a column vector and $\underline{\mathrm{a}}^{\dagger}$ as a row vector,

$$\underline{\mathrm{a}} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}; \tag{22.108}$$

$$\underline{\mathrm{a}}^{\dagger} = \begin{pmatrix} a_1^* \, a_2^* \, \cdots \end{pmatrix}, \tag{22.109}$$

such that

$$\underline{\rho} = \underline{\mathrm{a}}\underline{\mathrm{a}}^{\dagger} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} \begin{pmatrix} a_1^* \, a_2^* \, \cdots \end{pmatrix} = \begin{pmatrix} |a_1|^2 & a_1 a_2^* & \cdots \\ a_2 a_1^* & |a_2|^2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{22.110}$$

The density matrix is an *idempotent* operator since

$$\underline{\rho}^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \underline{\rho}\,. \tag{22.111}$$

Critical to the development is the equation for the time evolution of ρ,

$$i\hbar\frac{d\underline{\rho}}{dt} = i\hbar\frac{d}{dt}(\underline{\mathrm{a}}\underline{\mathrm{a}}^{\dagger}) = [\underline{\mathrm{H}}\underline{\mathrm{a}}\underline{\mathrm{a}}^{\dagger} - \underline{\mathrm{a}}(\underline{\mathrm{H}}\underline{\mathrm{a}})^{\dagger}] = \underline{\mathrm{H}}\underline{\rho} - \underline{\rho}\underline{\mathrm{H}} = [\underline{\mathrm{H}}, \underline{\rho}]\,. \tag{22.112}$$

Note that the sign is *different* from that in the evolution equation for the expectation values of operators,

$$i\hbar\frac{\langle\psi(t)|\hat{A}|\psi(t)\rangle}{dt} = \langle\psi(t)|[\hat{A}, \hat{H}]|\psi(t)\rangle\,. \tag{22.113}$$

I have suppressed the explicit time dependence in the amplitudes and operators in Eqs. (22.108)–(22.113). For the most part, I do not indicate such time dependence explicitly from this point onwards, although I retain it in some of the equations as a reminder.

As an example, consider a two-level atom interacting with an optical field in the RWA. In this case,

$$\underline{\mathrm{H}}(t) = \frac{\hbar}{2}\begin{pmatrix} -\omega_0 & \Omega_0^*(t)e^{i\omega t} \\ \Omega_0(t)e^{-i\omega t} & \omega_0 \end{pmatrix}, \tag{22.114}$$

and

$$i\hbar \begin{pmatrix} \dot{\rho}_{11} & \dot{\rho}_{12} \\ \dot{\rho}_{21} & \dot{\rho}_{22} \end{pmatrix} = \tfrac{\hbar}{2} \left[\begin{pmatrix} -\omega_0 & \Omega_0^*(t)e^{i\omega t} \\ \Omega_0(t)e^{-i\omega t} & \omega_0 \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} - \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} -\omega_0 & \Omega_0^*(t)e^{i\omega t} \\ \Omega_0(t)e^{-i\omega t} & \omega_0 \end{pmatrix} \right], \tag{22.115}$$

or, since $\chi(t) = \Omega_0(t)/2$,

$$\dot{\rho}_{11} = -i\chi^*(t)e^{i\omega t}\rho_{21} + i\chi(t)e^{-i\omega t}\rho_{12}\,; \tag{22.116a}$$

$$\dot{\rho}_{22} = i\chi^*(t)e^{i\omega t}\rho_{21} - i\chi(t)e^{-i\omega t}\rho_{12}\,; \tag{22.116b}$$

$$\dot{\rho}_{12} = i\omega_0\rho_{12} - i\chi^*(t)e^{i\omega t}\left(\rho_{22} - \rho_{11}\right)\,; \tag{22.116c}$$

$$\dot{\rho}_{21} = -i\omega_0\rho_{21} + i\chi(t)e^{-i\omega t}\left(\rho_{22} - \rho_{11}\right). \tag{22.116d}$$

One can solve these equations for a given $\chi(t)$, but it is easier to solve in the amplitude picture and then simply construct $\rho_{11}(t) = |a_1(t)|^2$, $\rho_{22}(t) = |a_2(t)|^2$, $\rho_{12}(t) = a_1(t)a_2^*(t)$, $\rho_{21}(t) = a_2(t)a_1^*(t)$. It looks like I have not gained *anything*, except making the equations more difficult! In a sense that is correct. The density matrix becomes useful and essential when dealing with ensembles of particles or particles interacting with a bath.

The key point is that it is often possible to get a simple equation for atomic density matrix elements that incorporates the effects of some thermal bath acting on the atoms. A general method for doing this is developed in the Appendix. For example, spontaneous emission results from an atom interacting with the vacuum field. Although the vacuum field plays a critical role in spontaneous decay, its net effect on *atomic* state density matrix elements is given simply by

$$\dot{\rho}_{11})_{sp} = \gamma_2\rho_{22}\,; \tag{22.117a}$$

$$\dot{\rho}_{22})_{sp} = -\gamma_2\rho_{22}\,; \tag{22.117b}$$

$$\dot{\rho}_{12})_{sp} = -\frac{\gamma_2}{2}\rho_{12}\,; \tag{22.117c}$$

$$\dot{\rho}_{21})_{sp} = -\frac{\gamma_2}{2}\rho_{21}\,. \tag{22.117d}$$

These contributions can be added to the terms given in Eqs. (22.116a)–(22.116d). Equation (22.107) loses its meaning once relaxation is introduced.

Including spontaneous decay,

$$\dot{\rho}_{11} = -i\chi^*(t)e^{i\omega t}\rho_{21} + i\chi(t)e^{-i\omega t}\rho_{12} + \gamma_2\rho_{22}\,; \tag{22.118a}$$

$$\dot{\rho}_{22} = i\chi^*(t)e^{i\omega t}\rho_{21} - i\chi(t)e^{-i\omega t}\rho_{12} - \gamma_2\rho_{22}\,; \tag{22.118b}$$

$$\dot{\rho}_{12} = i\omega_0\rho_{12} - i\chi^*(t)e^{i\omega t}\left(\rho_{22} - \rho_{11}\right) - \gamma\rho_{12}\,; \tag{22.118c}$$

$$\dot{\rho}_{21} = -i\omega_0\rho_{21} + i\chi(t)e^{-i\omega t}\left(\rho_{22} - \rho_{11}\right) - \gamma\rho_{21}\,, \tag{22.118d}$$

where

$$\gamma = \gamma_2/2. \tag{22.119}$$

Note that $\dot{\rho}_{11}(t) + \dot{\rho}_{22}(t) = 0$, consistent with conservation of population. Now I *have* gotten somewhere. It is impossible to write analogous equations using state amplitudes, since Eqs. (22.118) are already averaged over a thermal bath. Equations (22.118) are the starting point for many applications involving the interaction of radiation with matter.

The corresponding equations in the field-interaction representation are

$$\dot{\rho}_{11} = -i\left|\chi(t)\right|\tilde{\rho}_{21} + i\left|\chi(t)\right|\tilde{\rho}_{12} + \gamma_2\rho_{22}\,; \tag{22.120a}$$

$$\dot{\rho}_{22} = i\left|\chi(t)\right|\tilde{\rho}_{21} - i\left|\chi(t)\right|\tilde{\rho}_{12} - \gamma_2\rho_{22}\,; \tag{22.120b}$$

$$\dot{\tilde{\rho}}_{12} = i\delta(t)\tilde{\rho}_{12} - i\left|\chi(t)\right|\left(\rho_{22} - \rho_{11}\right) - \gamma\tilde{\rho}_{12}; \tag{22.120c}$$

$$\dot{\tilde{\rho}}_{21} = -i\delta(t)\tilde{\rho}_{21} + i\left|\chi(t)\right|\left(\rho_{22} - \rho_{11}\right) - \gamma\tilde{\rho}_{21}\,, \tag{22.120d}$$

where

$$\begin{aligned}\tilde{\rho}_{12} &= e^{-i[\omega t - \phi(t)]}\rho_{12}\,,\\ \tilde{\rho}_{21} &= e^{i[\omega t - \phi(t)]}\rho_{21}\,.\end{aligned} \tag{22.121}$$

Even if $|\chi(t)|$ and $\delta(t)$ are constant, it is not easy to obtain analytic solutions of Eqs. (22.120). You can eliminate $\rho_{11}(t)$ from the equations using $\rho_{11}(t) = 1 - \rho_{22}(t)$, but you are still faced with solving an auxiliary equation for the roots r of the trial solution, $\tilde{\rho}_{ij}(t) = \tilde{\rho}_{ij}(0)e^{rt}$, that is cubic. On the other hand, for constant χ and δ, it is a simple matter to obtain the *steady-state* solutions of these equations by setting the derivatives equal to zero. For constant $\chi = \Omega_0/2$ and δ, the steady-state population of the excited state is given by

$$\rho_{22} = \frac{\frac{2\gamma}{\gamma_2}|\chi|^2}{\delta^2 + \gamma_B^2}\,, \tag{22.122}$$

where

$$\gamma_B = \gamma\sqrt{1 + \frac{4|\chi|^2}{\gamma\gamma_2}}. \tag{22.123}$$

The excitation spectrum (that is, ρ_{22} as a function of δ) is a Lorentzian centered at $\delta = \omega_0 - \omega = 0$, having width (half-width at half-maximum) equal to γ_B. The fact that γ_B increases with increasing field intensity is referred to as *power broadening*.

22.4.1 Magnetic Bloch Equations

The off-diagonal density matrix elements are complex, in general, and cannot correspond to any measurable physical observable. However, it is possible to define real variables that correspond to physically measurable quantities. I do this first for the density matrix elements associated with an electron spin in a magnetic field and then for the density matrix elements for a two-level atom interacting with an optical field. For the magnetic case, I use the Schrödinger representation and, in the optical case, I use the field interaction representation. Both approaches lead to *Bloch equations* (named after Felix Bloch), but you will see that the field-interaction representation allows one to obtain a simple geometric picture of the quantum state evolution.

The Hamiltonian for the spin-magnetic field case is

$$\underline{H}_B = \frac{e}{m_e}\underline{\mathbf{S}} \cdot \mathbf{B} = \frac{e\hbar}{2m_e}\boldsymbol{\sigma} \cdot \mathbf{B} = \boldsymbol{\omega}_M \cdot \underline{\mathbf{S}}, \tag{22.124}$$

where

$$\boldsymbol{\omega}_M = \frac{e}{m_e}\mathbf{B} \tag{22.125}$$

is the *cyclotron frequency* and

$$\underline{\mathbf{S}} = \frac{\hbar}{2}\left[\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\mathbf{u}_\mathbf{x} + \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\mathbf{u}_\mathbf{y} + \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\mathbf{u}_\mathbf{z}\right]. \tag{22.126}$$

The density matrix associated with the two-component spin system is

$$\underline{\rho} = \begin{pmatrix}\rho_{\uparrow\uparrow} & \rho_{\uparrow\downarrow}\\ \rho_{\downarrow\uparrow} & \rho_{\downarrow\downarrow}\end{pmatrix}. \tag{22.127}$$

Since the spin operator corresponds to an angular momentum and is Hermitian, $\left\langle\hat{\mathbf{S}}\right\rangle = \hbar\left\langle\boldsymbol{\sigma}\right\rangle/2$ is real. Using

$$\left\langle\hat{\mathbf{S}}\right\rangle = \mathrm{Tr}\left(\underline{\rho}\underline{\mathbf{S}}\right) \tag{22.128}$$

with $\underline{\mathbf{S}}$ given by Eq. (22.126), you can show easily that

$$\left\langle \hat{S}_z \right\rangle = \frac{\hbar}{2}\left(\rho_{\uparrow\uparrow} - \rho_{\downarrow\downarrow}\right); \tag{22.129a}$$

$$\left\langle \hat{S}_x \right\rangle = \frac{\hbar}{2}\left(\rho_{\uparrow\downarrow} + \rho_{\downarrow\uparrow}\right); \tag{22.129b}$$

$$\left\langle \hat{S}_y \right\rangle = \frac{\hbar}{2}\left[i\left(\rho_{\uparrow\downarrow} - \rho_{\downarrow\uparrow}\right)\right]. \tag{22.129c}$$

If you can calculate the expectation value of the spin components, you can use Eqs. (22.129), along with conservation of probability, $\rho_{\uparrow\uparrow} + \rho_{\downarrow\downarrow} = 1$, to obtain the density matrix elements. Thus, specifying the expectation value of the spin components is equivalent to specifying the density matrix elements.

The time evolution of $\hat{\mathbf{S}}$ can be obtained from

$$\frac{d\left\langle \hat{\mathbf{S}} \right\rangle}{dt} = \frac{1}{i\hbar}\left\langle \left[\hat{\mathbf{S}}, \hat{H}_B\right]\right\rangle = \frac{1}{i\hbar}\left\langle \left[\hat{\mathbf{S}}, \boldsymbol{\omega}_M \cdot \hat{\mathbf{S}}\right]\right\rangle = \boldsymbol{\omega}_M \times \left\langle \hat{\mathbf{S}} \right\rangle. \tag{22.130}$$

The three equations represented by Eq. (22.130) are referred to as the magnetic Bloch equations. The vector $\left\langle \hat{\mathbf{S}} \right\rangle$ is the *Bloch vector*. Equation (22.130) is the same equation you would find for the components of a classical magnetic moment precessing in a magnetic field. Note that $\boldsymbol{\omega}_M$ can be an arbitrary function of time. For the magnetic field of Eq. (22.19), the x-component of $\boldsymbol{\omega}_M$ oscillates with frequency ω. For such a field, the axis about which the spin angular momentum is precessing is also oscillating as a function of time and it is not easy to get a simple picture of the dynamics.

22.4.2 Optical Bloch Equations

When the RWA is valid, as is often the case for fields driving optical transitions, it is possible to use the field interaction representation to remove the rapid oscillation of the precession axis associated with the frequency ω of the field. For a two-level atom, it is conventional to define real variables

$$\begin{aligned} u &= \tilde{\rho}_{12} + \tilde{\rho}_{21}; \\ v &= i\left(\tilde{\rho}_{21} - \tilde{\rho}_{12}\right); \\ w &= \rho_{22} - \rho_{11}; \\ m &= \rho_{22} + \rho_{11}, \end{aligned} \tag{22.131}$$

in terms of the density matrix elements in the field-interaction representation. The inverse transformation is

$$\begin{aligned}\tilde{\rho}_{12} &= \tfrac{u+iv}{2}\,;\\ \tilde{\rho}_{21} &= \tfrac{u-iv}{2}\,;\\ \rho_{11} &= \tfrac{m-w}{2}\,;\\ \rho_{22} &= \tfrac{m+w}{2}\,.\end{aligned} \tag{22.132}$$

Note that a matrix element such as $\rho_{12} = \tilde{\rho}_{12} e^{i[\omega t - \phi(t)]}$ can be written in terms of these variables as

$$\rho_{12} = (u + iv) e^{i[\omega t - \phi(t)]}/2. \tag{22.133}$$

It is especially important not to forget that the variables (u, v) are related to density matrix elements in the *field-interaction* representation. In calculating expectation values of operators, it is necessary to convert back to the Schrödinger representation.

In the absence of relaxation, it follows from these definitions and Eqs. (22.120) that

$$\begin{aligned}\dot{u} &= -\delta(t) v\,;\\ \dot{v} &= \delta(t) u - |\Omega_0(t)|\, w;\\ \dot{w} &= |\Omega_0(t)|\, v\,;\\ \dot{m} &= 0\,.\end{aligned} \tag{22.134}$$

Conservation of probability is expressed by the relation $m = 1$. If I construct column vectors

$$\mathbf{\Omega}(t) = \begin{pmatrix} |\Omega_0(t)| \\ 0 \\ \delta(t) \end{pmatrix}, \tag{22.135}$$

and

$$\mathcal{B} = \begin{pmatrix} u \\ v \\ w \end{pmatrix}, \tag{22.136}$$

Eq. (22.134) takes the vectorial form

$$d\mathcal{B}/dt = \mathbf{\Omega}(t) \times \mathcal{B}\,. \tag{22.137}$$

The vector $\mathcal{B}$ is referred to as the *optical Bloch vector*, the vector $\mathbf{\Omega}(t)$ is referred to as the *pseudofield vector*, and Eq. (22.137) is referred to as the *optical Bloch equation.*

The elements of the Bloch vector have a simple interpretation. The quantity m is the total population of the levels and w is the population difference. For the electric dipole transitions under consideration, u and v correspond to components of the

atomic dipole moment that are in-phase and out-of-phase with the applied field. One often refers to u and v (as well as $\tilde{\rho}_{12}$ and $\tilde{\rho}_{21}$) as "coherence." There is a simple geometric interpretation of Eq. (22.137) as well. The Bloch vector $\mathcal{B}$ precesses about the pseudofield vector $\mathbf{\Omega}(t)$ with angular frequency

$$\Omega(t) = \sqrt{\delta(t)^2 + |\Omega_0(t)|^2}.$$

Often it is easy to picture the dynamics produced by the interaction using the Bloch vector.

Since $\mathcal{B}$ precesses about the pseudofield vector, its magnitude must remain constant. I can show this explicitly by using Eq. (22.137) to write

$$\frac{d}{dt}|\mathcal{B}|^2 = \frac{d}{dt}(\mathcal{B}\cdot\mathcal{B}) = 2\mathcal{B}\cdot\frac{d\mathcal{B}}{dt} = 2\mathcal{B}\cdot[\mathbf{\Omega}(t)\times\mathcal{B}] = 0\,. \tag{22.138}$$

Therefore

$$|\mathcal{B}|^2 = u^2 + v^2 + w^2 = \text{constant}\,. \tag{22.139}$$

With the definitions given in Eqs. (22.131), I find

$$\begin{aligned} |\mathcal{B}|^2 &= u^2 + v^2 + w^2 \\ &= \tilde{\rho}_{12}^2 + 2\tilde{\rho}_{12}\tilde{\rho}_{21} + \tilde{\rho}_{21}^2 - \tilde{\rho}_{12}^2 + 2\tilde{\rho}_{12}\tilde{\rho}_{21} - \tilde{\rho}_{21}^2 + \rho_{22}^2 - 2\rho_{22}\rho_{11} + \rho_{11}^2 \\ &= \rho_{22}^2 + 2\rho_{22}\rho_{11} + \rho_{11}^2 = (\rho_{22} + \rho_{11})^2 = 1\,, \end{aligned} \tag{22.140}$$

where the relationship $\tilde{\rho}_{12}\tilde{\rho}_{21} = |\tilde{c}_1|^2|\tilde{c}_2|^2 = \rho_{11}\rho_{22}$ was used. Note that this relationship is valid only in the *absence* of any relaxation, allowing me to set $\tilde{\rho}_{12} = \tilde{c}_1\tilde{c}_2{}^* = \tilde{\rho}_{21}^*$. Since the magnitude of $\mathcal{B}$ is unity, the Bloch vector traces out a curve on the surface of the *Bloch sphere*, a sphere having radius unity in u, v, w space.

As a simple example consider the case when $\delta(t) = 0$ and $|\Omega_0| = \text{constant}$, with initial conditions $\rho_{11}(0) = 1$ $[\tilde{\rho}_{12}(0) = \tilde{\rho}_{21}(0) = \rho_{22}(0) = 0]$. This implies that $u(0) = v(0) = 0$ and $w(0) = -1$, see Fig. 22.3. Since $\Omega = |\Omega_0|\mathbf{u}_u$, it follows that $\mathcal{B}$ precesses about the u-axis with frequency $|\Omega_0|$, namely

$$\begin{aligned} u(t) &= 0\,; \\ v(t) &= \sin(|\Omega_0|t)\,; \\ w(t) &= -\cos(|\Omega_0|t)\,. \end{aligned} \tag{22.141}$$

If, instead, $|\Omega_0(t)|$ corresponds to a time-varying pulse envelope whose amplitude vanishes for $t < 0$, the precession phase angle at any time is given by

$$A(t) = \int_0^t |\Omega_0(t')|dt'. \tag{22.142}$$

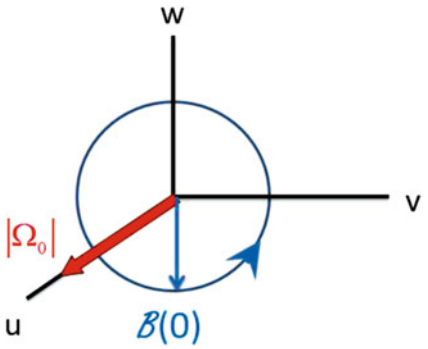

Fig. 22.3 When $\delta(t) = 0$ and $|\Omega_0|$ =constant, the Bloch vector $\mathcal{B}(t)$ rotates in the (w, v) plane with angular velocity $|\Omega_0|$

For this field, Eqs. (22.141) are replaced by

$$\begin{aligned} u(t) &= 0\,; \\ v(t) &= \sin A(t)\,; \\ w(t) &= -\cos A(t)\,, \end{aligned} \tag{22.143}$$

where $A(t)$ can be viewed as the pulse area at time t [see Eq. (22.76)]. For times when $A = \pi$, the population is completely inverted ($w = 1$), while for times when $A = \pm\pi/2$ the coherence is at a maximum ($|v| = 1$). Additional examples are given in the problems and the next chapter.

22.4.3 *Selection Rules for Electric Dipole and Magnetic Dipole Transitions*

You can use what you have learned about irreducible tensor operators and the Wigner-Eckart theorem to derive *selection rules* for electric dipole and magnetic dipole transitions. The selection rules tell you what states can be coupled by these interactions. For the sake of definiteness, I assume the eigenkets of an atom in the absence of the atom–field interactions can be written as $|nLSIJFm_F\rangle$, where n labels the electronic state manifold. In other words, I assume a Russell-Saunders coupling scheme in which the total orbital and spin angular momenta remain good quantum numbers.

22.4.3.1 Electric Dipole Transitions

The electric dipole interaction is given by Eq. (22.46), namely

$$\hat{H}'_e = -\hat{\mathbf{p}}_e \cdot \mathbf{E}(\mathbf{R}, t), \tag{22.144}$$

where $\hat{\mathbf{p}}_e$ is the electric dipole moment operator of the atom. To derive selection rules, I must determine which of the matrix elements

$$\left\langle n'L'S'IJ'F'm'_F \right| \hat{\mathbf{p}}_e \left| nLSIJFm_F \right\rangle \tag{22.145}$$

are non-vanishing. Since $\hat{\mathbf{p}}_e$ is a vector operator that can be written in terms of the components of an irreducible tensor of rank 1, it follows from the Wigner-Eckart theorem and the properties of the Clebsch-Gordan coefficients that this matrix element vanishes unless $\Delta F = F' - F = \pm 1, 0$, and that any $F = F' = 0$ matrix element also vanishes. Furthermore if I use the Clebsch-Gordan coefficients to expand $|nLSIJFm_F\rangle$ in terms of $|nLSJm_J\rangle\,|I\,m_I\rangle$ eigenkets, it also follows that a second selection rule is $\Delta J = \pm 1, 0$ and $J = 0 \rightarrow 0$ transitions are forbidden. The reason for this is that the operator $\hat{\mathbf{p}}_e$ depends only on spatial coordinates and must be diagonal in the nuclear spin quantum numbers. Continuing the development by expanding $|nLSJm_J\rangle$ in terms of $|nLm_L\rangle\,|Sm_S\rangle$ eigenkets, I arrive at the selection rules $\Delta S = 0$, $\Delta L = \pm 1, 0$. However, since $\hat{\mathbf{p}}_e$ is an odd parity operator, L must change by an odd integer—$\Delta L = 0$ is ruled out. To summarize, for the electric dipole matrix elements to be non-vanishing, the selection rules $\Delta F = \pm 1, 0$, $\Delta J = \pm 1, 0$, $\Delta S = 0$, and $\Delta L = \pm 1$ must be satisfied, with $F = 0 \rightarrow 0$ and $J = 0 \rightarrow 0$ transitions also forbidden.

It also follows from the Wigner-Eckart theorem and the properties of the Clebsch-Gordan coefficients that the selection rules for the azimuthal quantum numbers are $\Delta m_F = \pm 1, 0$. The relative contribution of the $\Delta m_F = \pm 1, 0$ matrix elements depends on the *polarization* of the electric field. I take the electric field to be of the form

$$\mathbf{E}(\mathbf{R}, t) = \frac{1}{2} E_0 \boldsymbol{\epsilon} e^{i(\mathbf{k}\cdot\mathbf{R} - \omega t)} + \frac{1}{2} E_0 \boldsymbol{\epsilon}^* e^{-i(\mathbf{k}\cdot\mathbf{R} - \omega t)}, \tag{22.146}$$

which corresponds to a classical monochromatic field propagating in the $\mathbf{k}$ direction. You can show that this field satisfies Maxwell's equations in vacuum provided $\omega = kc$ and $\mathbf{k} \cdot \boldsymbol{\epsilon} = 0$. I have taken the field amplitude E_0 to be real, but the field polarization

$$\boldsymbol{\epsilon} = \epsilon_x \mathbf{u}_x + \epsilon_y \mathbf{u}_y + \epsilon_x \mathbf{u}_z \tag{22.147}$$

can be complex. I will restrict the discussion to optical fields which resonantly couple different electronic levels, $n \neq n'$.

Let us imagine that the field couples a state $|n_1 F_1 m_{F_1}\rangle$ to a state $|n_2 F_2 m_{F_2}\rangle$ in an atom located at position $\mathbf{R}$ and that the energy of state 2 is greater than that of state

1 (all other state labels have been suppressed). In the interaction representation, the state amplitude c_2 evolves according to

$$\begin{aligned}\dot{c}_2 &= \frac{1}{i\hbar}\left\langle n_2F_2m_{F_2}\right|\hat{H}'_e\left|n_1F_1m_{F_1}\right\rangle e^{i\omega_0 t}c_1 \\ &= \frac{i}{2\hbar}\left\langle n_2F_2m_{F_2}\right|\boldsymbol{\epsilon}\cdot\hat{\mathbf{p}}_e\left|n_1F_1m_{F_1}\right\rangle E_0 e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\delta t}c_1,\end{aligned} \tag{22.148}$$

where I have made the RWA approximation by neglecting a term rapidly oscillating at the sum frequency $\omega + \omega_0$. This equation will allow me to determine the Δm_F selection rules for specific field polarizations.

To do so, I write

$$\boldsymbol{\epsilon}\cdot\hat{\mathbf{p}}_e = \sum_{q=-1}^{1}(-1)^q\epsilon_{-q}\hat{p}_{e,q}, \tag{22.149}$$

where

$$\hat{p}_{e,\pm1} = \mp(\hat{p}_{e,x} \pm i\hat{p}_{e,y})/\sqrt{2}; \tag{22.150a}$$

$$\hat{p}_{e,0} = \hat{p}_z. \tag{22.150b}$$

and

$$\epsilon_{\pm1} = \mp\frac{\epsilon_x \pm i\epsilon_y}{\sqrt{2}}; \tag{22.151a}$$

$$\epsilon_0 = \epsilon_z. \tag{22.151b}$$

I consider three field polarizations, *linearly polarized light* with

$$\epsilon_x^{\text{lp}} = \epsilon_y^{\text{lp}} = \epsilon_{\pm1}^{\text{lp}} = 0; \quad \epsilon_0^{\text{lp}} = 1; \quad \mathbf{k} = k\mathbf{u}_x, \tag{22.152}$$

left-circularly polarized light (LCP) with

$$\epsilon_x^{\text{lcp}} = \sqrt{\frac{1}{2}}; \quad \epsilon_y^{\text{lcp}} = i\sqrt{\frac{1}{2}}; \quad \epsilon_1^{\text{lcp}} = 0; \quad \epsilon_{-1}^{\text{lcp}} = 1; \quad \epsilon_0^{\text{lcp}} = 0; \quad \mathbf{k} = k\mathbf{u}_z, \tag{22.153}$$

and *right-circularly polarized light* (RCP) with

$$\epsilon_x^{\text{rcp}} = \sqrt{\frac{1}{2}}; \quad \epsilon_y^{\text{rcp}} = -i\sqrt{\frac{1}{2}}; \quad \epsilon_1^{\text{rcp}} = -1; \quad \epsilon_{-1}^{\text{rcp}} = 0; \quad \epsilon_0^{\text{rcp}} = 0; \quad \mathbf{k} = k\mathbf{u}_z. \tag{22.154}$$

In the case of linear polarization, the field propagates in the X-direction and the electric field is

$$\mathbf{E}^{\rm lp}(\mathbf{R},t) = E_0 \cos\left(kX - \omega t\right) \mathbf{u}_z, \tag{22.155}$$

while, for circular polarization, the field propagates in the Z-direction and electric field is

$$\mathbf{E}^{\rm lcp}(\mathbf{R},t) = \frac{1}{\sqrt{2}} E_0 \left[\mathbf{u}_x \cos\left(kZ - \omega t\right) - \mathbf{u}_y \sin\left(kZ - \omega t\right)\right]; \tag{22.156a}$$

$$\mathbf{E}^{\rm rcp}(\mathbf{R},t) = \frac{1}{\sqrt{2}} E_0 \left[\mathbf{u}_x \cos\left(kZ - \omega t\right) + \mathbf{u}_y \sin\left(kZ - \omega t\right)\right]. \tag{22.156b}$$

Left circular polarization radiation has angular momentum directed *along* its propagation direction. When viewed "head-on" with the radiation approaching you, the polarization vector has constant amplitude and rotates in a counterclockwise direction. Right circular polarization (RCP) radiation has angular momentum directed *opposite* to its propagation direction. When viewed "head-on" with the radiation approaching you, the polarization has constant amplitude rotates in a clockwise direction. Note that the polarization given in Eq. (22.153) would correspond to LCP and that in Eq. (22.154) to RCP if the field propagates in the $-Z$ direction.

Now that I have written the interaction in terms of the irreducible components of the electric dipole operator, I can use Eqs. (22.148)–(22.154) and the Wigner-Eckart theorem to evaluate

$$\begin{aligned}
&\langle n_2 F_2 m_{F_2}| \sum_{q=-1}^{1} (-1)^q \epsilon_{-q} \hat{p}_{e,q} \, |n_1 F_1 m_{F_1}\rangle \\
&\quad = \sum_q (-1)^q \langle n_2 F_2 || p_e^{(1)} || n_1 F_1 \rangle \\
&\qquad \times \frac{\epsilon_{-q}}{\sqrt{2F_2+1}} \begin{bmatrix} F_1 & 1 & F_2 \\ m_{F_1} & q & m_{F_2} \end{bmatrix},
\end{aligned} \tag{22.157}$$

from which it follows that the selection rules on absorption are:

$$\Delta m_F = 0 \quad \text{linear polarization;} \tag{22.158a}$$

$$\Delta m_F = 1 \quad \text{LCP with } \mathbf{k} = k\mathbf{u}_z; \ \text{RCP with } \mathbf{k} = -k\mathbf{u}_z; \tag{22.158b}$$

$$\Delta m_F = -1 \quad \text{RCP with } \mathbf{k} = k\mathbf{u}_z; \ \text{LCP with } \mathbf{k} = -k\mathbf{u}. \tag{22.158c}$$

The signs are reversed for emission, that is, for transitions from a higher to lower energy state in the RWA.[2]

[2]Had I *not* made the RWA, the selection rules for LCP and RCP resulting from the rapidly varying term would be reversed from those of the resonant term.

22.4.3.2 Magnetic Dipole Transitions

The magnetic dipole interaction is given by

$$\hat{H}'_m = -(\hat{\mathbf{m}}_L + \hat{\mathbf{m}}_s)\cdot\mathbf{B}(\mathbf{R},t) = \frac{\beta_0 B}{\hbar}\left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right)\cdot\mathbf{B}(\mathbf{R},t), \tag{22.159}$$

Since $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are vector operators, the selection rules for ΔF and ΔJ are the same as those for electric dipole transitions, namely $\Delta F = \pm 1, 0$, $\Delta J = \pm 1, 0$, with $F = 0 \rightarrow 0$ and $J = 0 \rightarrow 0$ transitions also forbidden. The selection rule on spin angular momentum is still $\Delta S = 0$ since the interaction cannot change the magnitude of the spin; however, the selection rule for ΔL is now $\Delta L = 0$, since the interaction (22.159) couples only those states having the *same* parity. Moreover, since the interaction does not depend on spatial operators such as $\hat{\mathbf{p}}_e$, there is now a selection rule on n, $\Delta n = 0$. Magnetic fields couple only those states *within* a given electronic state manifold. The selection rules for Δm_F are unchanged from the electric dipole case, except that it may no longer be a good approximation to make the RWA for radio-frequency fields that drive transitions between different hyperfine states.

22.5 Summary

In this chapter, I presented an introduction to problems that can be categorized as *semi-classical*, in which a classical time-dependent field interacts with a quantum system. Some general results were derived and specific examples were given related to the interaction of a magnetic field with a spin 1/2 quantum system and an optical field with a two-level atom. The concept of the density matrix was introduced and the Bloch equations were derived.

22.6 Appendix: Interaction of an Atom with a Thermal Bath

Consider what happens when a single atom interacts with a thermal bath. The total Hamiltonian is

$$\hat{H}=\hat{H}_1+\hat{H}_2+\hat{V}\,, \tag{22.160}$$

where $\hat{H}_1$ is the Hamiltonian of the atomic system (possibly including interactions with time-dependent external fields), $\hat{H}_2$ is the time-independent Hamiltonian of the bath, and $\hat{V}$ is the atom–bath interaction energy. The eigenkets of the time-independent part of $\hat{H}_1$ are denoted by $|n_1\rangle$ and the eigenkets of $\hat{H}_2$ are denoted by

$|n_2\rangle$. Suppose we have an operator $\hat{A}_1$ that acts *only* in the space of $\hat{H}_1$; that is, $\hat{A}_1$ acts only on atomic state variables. For a wave function

$$|\psi(t)\rangle = \sum_{n_1,n_2} a_{n_1 n_2}(t)|n_1\rangle|n_2\rangle\,, \tag{22.161}$$

I calculate

$$\begin{aligned}\langle\hat{A}_1\rangle = \langle\psi|\hat{A}_1|\psi\rangle &= \sum_{n_1,n_2}\sum_{n_1',n_2'} a^*_{n_1 n_2} a_{n_1' n_2'}\langle n_1|\langle n_2|\hat{A}_1|n_2'\rangle|n_1'\rangle \\ &= \sum_{n_1,n_2}\sum_{n_1',n_2'} a^*_{n_1 n_2} a_{n_1' n_2'}\delta_{n_2,n_2'}\langle n_1|\hat{A}_1|n_1'\rangle\end{aligned} \tag{22.162}$$

or

$$\langle\psi|\hat{A}_1|\psi\rangle = \sum_{n_1,n_1'} (A_1)_{n_1 n_1'}\left(\sum_{n_2} a^*_{n_1 n_2} a_{n_1' n_2}\right)\,. \tag{22.163}$$

I define the *reduced density matrix* for the atom as the total density matrix, traced over the states of the bath,

$$\underline{\rho}^{(1)} = \mathrm{Tr}_2\underline{\rho}; \tag{22.164}$$

that is,

$$\rho^{(1)}_{nn'} = \sum_{n_2}\rho_{nn_2;n'n_2} = \sum_{n_2} a_{nn_2}a^*_{n'n_2}\,. \tag{22.165}$$

It is clear from Eqs. (22.163) and (22.165) that

$$\langle\hat{A}_1\rangle = \sum_{n_1,n_1'}(A_1)_{n_1 n_1'}\rho^{(1)}_{n_1' n_1} = \mathrm{Tr}(\underline{A}_1\underline{\rho}^{(1)})\,. \tag{22.166}$$

The key point is that it is often possible to get a simple equation for $\underline{\rho}^{(1)}$ that incorporates the effects of the bath. For example, I show explicitly in Chap. 24 that the result of spontaneous emission is to introduce terms in the equations of motion for the reduced density matrix elements for the atom given by Eqs. (22.120). One can also consider the bath as an ensemble of perturber atoms that collide with the atom of interest. The collisions cause sudden changes in energy of the various levels, but are not energetically able to cause transitions between the two levels. In this model,

$$\dot{\rho}_{11}(t)_{\mathrm{coll}} = 0\,; \tag{22.167a}$$

$$\dot{\rho}_{22}(t)_{\text{coll}} = 0\,; \tag{22.167b}$$

$$\dot{\rho}_{12}(t)_{\text{coll}} = -(\Gamma + iS)\,\rho_{12}(t)\,; \tag{22.167c}$$

$$\dot{\rho}_{21}(t)_{\text{coll}} = -(\Gamma - iS)\,\rho_{21}(t)\,, \tag{22.167d}$$

where Γ is a decay rate and S is a shift, both of which are proportional to the perturber density. The collision effects can be incorporated into Eqs. (22.118) and (22.120) by replacing γ with $\gamma_2/2 + (\Gamma + iS)$ in Eqs. (22.118c) and (22.120c) and γ with $\gamma_2/2 + (\Gamma - iS)$ in Eqs. (22.118d) and (22.120d) and can be incorporated into Eq. (22.122) by replacing δ with $\delta - S$ and γ with $\gamma_2/2 + \Gamma$.

22.7 Problems

1. In time-dependent problems, the Hamiltonian is often taken to be of the form $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$. On average, is energy conserved for this Hamiltonian? Explain. Even if $\hat{H}_0$ consists of only two states (such as for a spin 1/2 system), why is it impossible, in general, to solve for the state amplitudes analytically given some initial conditions. What are some general conditions on $\hat{V}(t)$ if it is to effectively cause transitions between two states of $\hat{H}_0$.

2. Two *degenerate* states, 1 and 2, are coupled by a *constant* interaction potential, $\langle 1|\,\hat{V}\,|2\rangle = \langle 2|\,\hat{V}\,|1\rangle = V_{12} =$constant. If at $t = 0$, the system is in state 1, find the probability amplitudes for the system to be in state 1 and in state 2 for all $t > 0$. Assume that $V_{11} = V_{22} = 0$.

3–4. In dimensionless units, the equations for the probability amplitudes for a spin 1/2 system in an oscillating magnetic field are given by

$$d\mathbf{a}_B(\tau)/d\tau = -i\begin{pmatrix} x/2 & z\cos(y\tau) \\ z\cos(y\tau) & -x/2 \end{pmatrix}\mathbf{a}_B(\tau)$$

where $\mathbf{a}_B = (a_\uparrow, a_\downarrow)$, $x = \omega_0 T; y = \omega T; z = \omega_x T$, and $\tau = t/T$. Use a computer program such as NDSolve in Mathematica to obtain and plot solutions for $P_{up}(\tau) = \left|a_\uparrow(\tau)\right|^2$ as a function of τ for

i. $\omega T = 0;\ \omega_x T = 0.5, 1, 2, 10;\ \omega_0 T = 5;$

ii. $\omega T = 2;\ \omega_x T = 0.5, 1, 2, 10;\ \omega_0 T = 0;$

iii. $\omega T = 10;\ \omega_x T = 0.5, 1, 2, 10;\ \omega_0 T = 10,$

given $a_\uparrow(0) = 0; a_\downarrow(0) = 1$. In each case, are there single or multiple frequencies present in $P_{up}(\tau)$?

5–6. Consider a *classical* spin having magnetic moment $\mathbf{m}_s = -e\mathbf{S}/m_e$ where $\mathbf{S}$ is a spin angular momentum. In an external magnetic field $\mathbf{B}$ the spin experiences a torque

$$\boldsymbol{\tau} = \frac{d\mathbf{S}}{dt} = \mathbf{m}_s \times \mathbf{B}.$$

Show that the equation for the spin angular momentum is

$$\frac{d\mathbf{S}}{dt} = \boldsymbol{\omega}_B \times \mathbf{S},$$

where

$$\boldsymbol{\omega}_B = \frac{e\mathbf{B}}{m_e}.$$

Write the differential equation for the spin in component form.

Now take

$$\boldsymbol{\omega}_B = \omega_0 \mathbf{u}_z + \omega_s \cos(\omega t)\, \mathbf{u}_x$$

and solve numerically and plot S_z as a function of time with initial condition $S_z(0) = -1$ (in arbitrary units). Take time to have dimensionless units, $\tau = t/T$, and consider two cases (i) $\omega_0 T = 10$, $\omega_s T = 1$, $\omega T = 6$ (off-resonant) and (ii) $\omega_0 T = 10$, $\omega_s T = 1$, $\omega T = 10$ (resonant). What is the difference between the two cases? Also plot $S_x(t)$ for the resonant case with the same initial conditions; in this case you will see that there are rapid oscillations in $S_x(t)$ even though the rotating-wave approximation is valid—you need to go to a rotating frame (field interaction representation) to remove these rapid oscillations.

7–8. The optical Bloch equations with decay for a monochromatic field are

$$\begin{aligned}
\dot{u} &= -\delta v - \gamma u\,; \\
\dot{v} &= \delta u - |\Omega_0| w - \gamma v\,; \\
\dot{w} &= |\Omega_0| v - \gamma_2 (w+1); \\
\dot{m} &= 0\,,
\end{aligned}$$

where $\gamma = \gamma_2/2$. Derive these equations starting from Eqs. (22.131) and (22.120). Solve these equations in steady-state. Look at the results in the limit that $\Omega_0 \gg \gamma_2$ and interpret your result. In particular show that the expression for the steady-state, upper state population, $\rho_{22} = (1+w)/2$, is a Lorentzian having HWHM $\sqrt{\gamma^2 + \frac{\Omega_0^2}{2}}$; since the width increases with increasing field intensity, this is known as *power broadening*.

9. Now solve the Bloch equations of Problem 22.7–8 numerically for $\gamma T = \gamma_2 T/2 = 1/2$ and ($\delta T = 0.1$, $\Omega_0 T = 0.2$) and ($\delta T = 0.1$, $\Omega_0 T = 3$) and plot w as a function of dimensionless time $\tau = t/T$, assuming the atom is initially in its ground state. In which case does the Bloch vector approach its steady-state value monotonically? Why would you expect this from the Bloch vector picture?

10–11. Assuming a constant field amplitude, solve Eqs. (22.120) analytically for $\gamma = \gamma_2/2$, $\delta = 0$, and $\rho_{11}(0) = 1$ to show that the upper state population is given by

$$\rho_{22}(t) = \frac{|\Omega_0|^2/2}{2\gamma^2 + |\Omega_0|^2}\{1 - [\cos(\lambda t) + \frac{3\gamma}{2\lambda}\sin(\lambda t)]e^{-3\gamma t/2}\},$$

where $\lambda = (|\Omega_0|^2 - \gamma^2/4)^{1/2}$. Evaluate ρ_{22} for $|\Omega_0| \gg \gamma$ and give an interpretation in terms of the Bloch vector. Show that, as $t \to \infty$, result is consistent with Problem 22.7–8.

12. In the *field interaction representation*, neglecting relaxation, the state vector can be written quite generally as

$$|\psi(t)\rangle = \sin(\theta/2)\left|\tilde{1}(t)\right\rangle + \cos(\theta/2)e^{-i\phi}\left|\tilde{2}(t)\right\rangle,$$

where θ and ϕ are arbitrary real functions of time with $0 \le \theta \le \pi$ and $0 \le \phi \le 2\pi$. Show that the angles θ and ϕ correspond to the spherical angles of the Bloch vector on the Bloch sphere.

13–15. Consider the differential equation $\dot{\mathbf{y}}(t) = \underline{\mathrm{A}}\mathbf{y}(t)$, where $\mathbf{y}(t)$ is a column vector and $\underline{\mathrm{A}}$ is a **constant** matrix.

(a) Show, by direct substitution, that a solution to this equation is $\mathbf{y}(t) = e^{\underline{\mathrm{A}}t}\mathbf{y}(0)$. In the following parts, take

$$\underline{\mathrm{A}} = -i\begin{pmatrix} -a & b \\ b & a \end{pmatrix}; \qquad \mathbf{y}(0) = \begin{pmatrix} y_1(0) \\ y_2(0) \end{pmatrix}; \qquad \mathbf{y}(t) = \begin{pmatrix} y_1(t) \\ y_2(t) \end{pmatrix},$$

where a and b are real.

(b) Solve the differential equation directly by assuming a solution of the form $\mathbf{y}(t) = \mathbf{y}e^{\lambda t}$.

(c) Solve the equations using the identity

$$e^{-i\theta\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}} = \mathbf{1}\cos\theta - i\,\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\sin\theta,$$

where $\hat{\mathbf{n}}$ is a unit vector and $\boldsymbol{\sigma}$ is a vector having matrix components

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \qquad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \qquad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

(d) Solve the equation using the MatrixExp[{{$I\,a$,$-I\,b$},{$-I\,b$,$-I\,a$}}] function of Mathematica or some equivalent program.

(e) Find a matrix $\underline{\mathrm{T}}$ such that $\underline{\mathrm{T}}\,\underline{A}\,\underline{\mathrm{T}}^{\dagger} = \underline{\Lambda}$, where $\underline{\Lambda} = \begin{pmatrix} \Lambda_1 & 0 \\ 0 & \Lambda_2 \end{pmatrix}$ is a diagonal matrix. Prove that

$$\mathbf{y}(t) = \underline{\mathrm{T}}^{\dagger} e^{\underline{\Lambda} t}\underline{\mathrm{T}}\mathbf{y}(0) = \underline{\mathrm{T}}^{\dagger}\begin{pmatrix} e^{\Lambda_1 t} & 0 \\ 0 & e^{\Lambda_2 t} \end{pmatrix}\underline{\mathrm{T}}\mathbf{y}(0),$$

and evaluate this explicitly.

(f) Show that all your results give the same solution. Note that the last method can be used for matrices of any dimension.

16. Imagine that a circularly polarized field drives a $J = 0$ to $J = 1$ transition in an atom. At the atomic position, $Z = 0$, take the field to be of the form

$$\mathbf{E}(t) = E_0\left[\mathbf{u}_x \cos(\omega t) + \mathbf{u}_y \sin(\omega t)\right],$$

where E_0 is constant. Prove that, if one considers transitions between the $J = 0$ and $J = 1, m_J = 1$ levels only, it is *not* necessary to make any RWA to arrive at equations of the form in Eq. (22.65). On the other hand, show that the "counter-rotating" (rapidly oscillating) terms drive transitions between the $J = 0$ and $J = 1, m_J = -1$ levels. If the field is far off-resonance, both transitions contribute comparable amounts to the atomic response.