6 THE TIME-DEPENDENT SCHRÖDINGER EQUATION

6.1 INTRODUCTION

The stationary-state solutions $\Phi_n(\mathbf{r})$ obtained for a potential $V(\mathbf{r})$ determine the state probability distributions of particles in specific energy states. The orbit associated with any given energy E_n is not like a classical orbit; it is not a trajectory in space. Instead it is a spread-out region of more or less concentrated probability. The orbit is static; it is a probability distribution fixed in time.

Energy can be imparted to or taken from a quantum system only if the system can jump from one energy E_m to another energy E_n, i.e., only if it can change its orbit. A change from one orbit to another can occur if an external time-dependent force $\mathbf{F}_{\text{ext}}$ acts on the quantum system.

We can associate this force with a new potential energy in the usual way:

$$\mathbf{F}_{\text{ext}}(\mathbf{r}, t) = -\nabla V_{\text{ext}}(\mathbf{r}, t).$$

Then the system's total energy function (Hamiltonian) can be altered to account for the new force by adding V_{ext}:

$$H = H_a + V_{\text{ext}}(\mathbf{r}, t) \tag{6.1.1}$$

Here we are using the subscript a to mean atomic, and by H_a we mean the Hamiltonian function given in (5.3.5) which describes an atomic particle bound by the potential $V(\mathbf{r})$. The new total Hamiltonian $H(\mathbf{p}, \mathbf{r}, t)$ incorporates the particle's kinetic energy $\mathbf{p}^2/2m$ and both the static binding potential $V(\mathbf{r})$ and the time-dependent external potential $V_{\text{ext}}(\mathbf{r}, t)$. The Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}, t)\right)\Psi(\mathbf{r}, t) = i\hbar\frac{\partial\Psi}{\partial t} \tag{6.1.2}$$

6.2 TIME-DEPENDENT SOLUTIONS

Since H is now time-dependent, the time-dependent part of the wave function of the system cannot be factored as in (5.3.4). This is discussed in Problem 6.1.

Another method of solution was proposed by P. A. M. Dirac around 1926. It makes use of the "completeness" of the orbital functions $\Phi_n(\mathbf{r})$, discussed in Section 5.4. Because the set $\Phi_n(\mathbf{r})$ is complete, any function can be written in terms of the Φ_n's, for example $\Psi(\mathbf{r}, t)$. Following Dirac, we write the exact (still unknown) time-dependent wave function as a sum of Φ_n's:

$$\Psi(\mathbf{r}, t) = \sum_n a_n \Phi_n(\mathbf{r}) \tag{6.2.1}$$

However, since Ψ changes in time, the specific set of coefficients a_n that can be used to reconstitute Ψ out of Φ_n's must also change in time. That is, the a's are also time-dependent.

Since Schrödinger's equation (6.1.2) is responsible for the time dependence of Ψ, it is also indirectly responsible for the time dependence of the a's. We can determine the equations for the a's as follows. First, we apply (6.1.2) to Ψ written as in (6.2.1):

$$\sum_n a_n [H_a + V_{\text{ext}}]\, \Phi_n(\mathbf{r}) = \sum_n i\hbar \frac{\partial a_n}{\partial t}\, \Phi_n(\mathbf{r}) \tag{6.2.2}$$

Next we use the fact that the set $\Phi_n(\mathbf{r})$ is the solution set for the time-independent Schrödinger equation (5.3.5). This means that $H_a \Phi_n = E_n \Phi_n$, so (6.2.2) can be rewritten as

$$\sum_n a_n [E_n + V_{\text{ext}}]\, \Phi_n(\mathbf{r}) = \sum_n i\hbar \frac{\partial a_n}{\partial t}\, \Phi_n(\mathbf{r}) \tag{6.2.3}$$

Next we take the projection of both sides of (6.2.3) along the function $\Phi_m(\mathbf{r})$. Here we understand projection in the sense explained in Section 5.4 [recall (5.4.7)]:

$$\langle \Phi_m | \Phi_n \rangle = \int_{\substack{\text{all}\\ \text{space}}} \Phi_m^*(\mathbf{r})\, \Phi_n(\mathbf{r})\, d^3r = \delta_{mn} \tag{6.2.4}$$

Thus we find

$$i\hbar \dot{a}_m = E_m a_m + \sum_n a_n \int \Phi_m^*(\mathbf{r})\, V_{\text{ext}} \Phi_n(\mathbf{r})\, d^3r \tag{6.2.5}$$

where we have used a dot to indicate time derivative and the definition (5.4.8) to evaluate the sums

$$\sum_n a_n E_n \langle \Phi_m | \Phi_n \rangle = a_m E_m$$

$$\sum_n i\hbar \dot{a}_n \langle \Phi_m | \Phi_n \rangle = i\hbar \dot{a}_m \tag{6.2.6}$$

The integration in (6.2.5) cannot yet be carried out, because the $\mathbf{r}$ dependence of V_{ext} has not been specified. However, the integral can be abbreviated conveniently as

$$V_{mn}(t) = \int \Phi_m^*(\mathbf{r})\, V_{\text{ext}}(\mathbf{r}, t)\, \Phi_n(\mathbf{r})\, d^3r \tag{6.2.7}$$

For reasons that are explained in the next black-dot section, V_{mn} is called the *matrix element* of V_{ext} between the states m and n of the atomic system. In terms of this matrix element, Eq. (6.2.5) takes a more compact form:

$$i\hbar \dot{a}_m = E_m a_m + \sum_n V_{mn}(t)\, a_n \tag{6.2.8}$$

This equation, as well as (6.1.2), is frequently called the *time-dependent Schrödinger equation*. This is reasonable, since knowledge of the a's, obtained by solving (6.2.8), can be used as in (6.2.1) to reconstitute the full $\Psi(\mathbf{r}, t)$.

The a's themselves are called *probability amplitudes*. This name follows from the normalization property of Ψ. According to the probability interpretation of quantum mechanics we must have

$$\int_{\substack{\text{all}\\ \text{space}}} \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\, d^3r = 1 \tag{6.2.9}$$

Therefore (6.2.1) implies

$$\begin{aligned} \int \left(\sum_m a_m \Phi_m\right)^* \left(\sum_n a_n \Phi_n\right) d^3r &= 1 \\ &= \sum_m a_m^* \sum_n a_n \langle \Phi_m | \Phi_n \rangle \\ &= \sum_m \sum_n a_m^* a_n \delta_{mn} \\ &= \sum_m |a_m|^2 = 1 \end{aligned} \tag{6.2.10}$$

It is natural to identify each term in (6.2.10) as an orbital probability. That is, the squared magnitude $|a_m|^2$ is the probability that the quantum system (for example, the atomic electron) is in its mth orbit. The term probability amplitude is then used for a_m itself.

There is a significant shift in viewpoint between (6.2.9) and (6.2.10) even though they express the same normalization. Recall that $|\Psi(\mathbf{r}, t)|^2\, d^3r$ is the electron probability assigned to the differential volume element d^3r. There is no information about orbitals in this assignment, and indeed, many or all of the orbitals may make a contribution to the probability within d^3r. On the other hand,

$|a_m|^2$ plays the opposite role. It is the probability that the electron is in the mth orbital, without providing any information about the spatial location of the electron in that orbit. In laser physics information about orbital occupation by the atomic electron is much more useful than information about its spatial location. For this reason we will concentrate completely on solutions of the second form of the time-dependent Schrödinger equation, given in (6.2.8).

- Let us write out the equations for the coefficients a_n in (6.2.8) in order, i.e.,

$$\begin{aligned} i\hbar\dot{a}_1 &= E_1 a_1 + V_{11}a_1 + V_{12}a_2 + V_{13}a_3 + \cdots \\ i\hbar\dot{a}_2 &= E_2 a_2 + V_{21}a_1 + V_{22}a_2 + V_{23}a_3 + \cdots \\ i\hbar\dot{a}_3 &= E_3 a_3 + V_{31}a_1 + V_{32}a_2 + V_{33}a_3 + \cdots \\ &\ \vdots \end{aligned} \tag{6.2.11}$$

We see that they can be written as a single *matrix equation*:

$$i\hbar\dot{\underline{\Psi}} = \underline{H\Psi} \tag{6.2.12}$$

where

$$\underline{\Psi} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \tag{6.2.13}$$

and

$$\underline{H} = \begin{bmatrix} E_1 + V_{11} & V_{12} & V_{13} & \cdots \\ V_{21} & E_{22} + V_{22} & V_{23} & \cdots \\ V_{31} & V_{32} & E_3 + V_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \tag{6.2.14}$$

This matrix form of the Schrödinger equation is the origin of the term "matrix element" for V_{nm}. In this form $\underline{H}$ is called the *Hamiltonian matrix* and $\underline{\Psi}$ the *state vector*. Heisenberg's original approach to quantum mechanics (1925) was through such matrices. Physical observables were represented by Hermitian matrices, whose matrix elements satisfy the relation $V^*_{nm} = V_{mn}$. It was not immediately appreciated that Heisenberg's "matrix mechanics" is equivalent to Schrödinger's "wave mechanics". •

6.3 TWO-STATE QUANTUM SYSTEMS AND SINUSOIDAL EXTERNAL FORCES

According to Bohr's description of quantum jumps, an atom can increase its energy by jumping from an orbit with energy E to one with higher energy E' if a photon of frequency ω is simultaneously absorbed, where $\hbar\omega = E' - E$. The reverse process is associated with the emission of a photon of frequency ω.

We associate photons of frequency ω with an electromagnetic wave of the same frequency. According to our analysis in Section 2.2, an external electromagnetic field interacts with an electron via the time-dependent potential

$$V_{\text{ext}}(\mathbf{r}, \mathbf{R}, t) = -e\mathbf{r} \cdot \mathbf{E}(\mathbf{R}, t)$$

We showed in Section 2.2 that $\mathbf{r}$ is the relative electron–nuclear distance and $\mathbf{R}$ is the location of the center of atomic mass. We will begin by considering a monochromatic plane wave for $\mathbf{E}$:

$$\begin{aligned} \mathbf{E}(\mathbf{R}, t) &= \hat{\varepsilon} E_0 \cos(\mathbf{k}\cdot\mathbf{R} - \omega t) \\ &= \tfrac{1}{2}\hat{\varepsilon} E_0\, e^{i(\mathbf{k}\cdot\mathbf{R} - \omega t)} + \text{c.c.} \\ &\to \tfrac{1}{2}\hat{\varepsilon} E_0 e^{-i\omega t} + \text{c.c.} \end{aligned} \tag{6.3.1}$$

where c.c. means complex conjugate and for convenience $\mathbf{R}$ has been put at the origin. This form of V_{ext} is the result of the dipole approximation, which is highly accurate when applied to optical transitions in atoms.

The implication of Bohr's rule for quantum jumps is that only pairs of energy levels in the atom that are separated by $\Delta E = \hbar\omega$ are affected by radiation present at frequency ω. Therefore, we will begin our study by restricting our attention to just two of the electronic energy levels. These are shown in Figure 6.1 and designated 1 and 2, with energies E_1 and E_2, such that $\Delta E = E_2 - E_1 = \hbar\omega$.

For such a two-state system the expression (6.2.1) is simply

$$\Psi(\mathbf{r}, t) = a_1(t)\,\Phi_1(\mathbf{r}) + a_2(t)\,\Phi_2(\mathbf{r}) \tag{6.3.2}$$

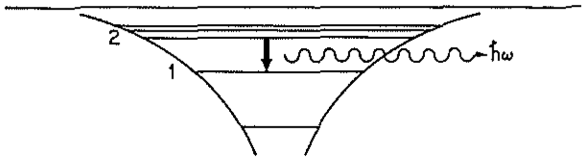

Figure 6.1 Energy levels of a hypothetical atom. Radiation of angular frequency ω is nearly resonant with the $E_1 \to E_2$ transition.

and the Schrödinger equation (6.2.8) reduces to

$$i\hbar\dot{a}_1(t) = E_1 a_1(t) + V_{11}a_1(t) + V_{12}a_2(t) \tag{6.3.3a}$$

$$i\hbar\dot{a}_2(t) = E_2 a_2(t) + V_{21}a_1(t) + V_{22}a_2(t) \tag{6.3.3b}$$

Level 1 may be the ground level but need not be. In most cases of interest the parity selection rule (see Problem 6.5) requires the diagonal matrix elements V_{11} and V_{22} of the interaction to be zero. Then

$$i\hbar\dot{a}_1(t) = E_1 a_1(t) + V_{12}a_2(t) \tag{6.3.4a}$$

$$i\hbar\dot{a}_2(t) = E_2 a_2(t) + V_{21}a_1(t) \tag{6.3.4b}$$

Equations (6.3.4) give the time variation of the probability amplitudes a_1 and a_2 for the two-state system. If the two-state model is a reasonable approximation we can assume that the system has negligible probability of being in any state other than Φ_1 or Φ_2. In other words, the probability that the system will be found in one or the other of these two states is unity at any time:

$$|a_1(t)|^2 + |a_2(t)|^2 = 1 \tag{6.3.5}$$

This is the two-state version of (6.2.10).

Equations (6.3.4) show how the 1–2 and 2–1 matrix elements of V_{ext} are involved in changes in the amplitudes $a_1(t)$ and $a_2(t)$. From (6.2.7) and (6.3.1) we can express these matrix elements more explicitly as

$$V_{12}(t) = -e\mathbf{r}_{12}\cdot\tfrac{1}{2}(\hat{\varepsilon}E_0 e^{-i\omega t} + \text{c.c.}) \tag{6.3.6}$$

$$V_{21}(t) = -e\mathbf{r}_{21}\cdot\tfrac{1}{2}(\hat{\varepsilon}E_0 e^{-i\omega t} + \text{c.c.}) \tag{6.3.7}$$

where, for example, the 1–2 matrix element of $\mathbf{r}$ is defined by

$$\mathbf{r}_{12} \equiv \int \Phi_1^*(\mathbf{r})\,\mathbf{r}\,\Phi_2(\mathbf{r})\,d^3r \tag{6.3.8}$$

Note that $\mathbf{r}_{12}$ is generally a complex-valued vector because the Φ's may be complex. The numerical value of $\mathbf{r}_{12}$ depends on the wave functions Φ_1 and Φ_2, so the size of the matrix elements V_{12} and V_{21} must be expected to vary from atom to atom. As a typical magnitude (associated with an optical transition to or from an atomic ground state), one can expect $|\mathbf{r}_{12}|$ to differ from the Bohr radius $a_0 \approx \frac{1}{2}$ Å by less than a factor of 10. Listings of the radial and angular parts of the coordinate matrix element $\mathbf{r}_{12}$ are given in Appendix 6.*A* for various transitions in hydrogen. Notice that the matrix element tends to have a significantly larger magnitude if the n values are different by only one unit.

With $V_{12}(t)$ and $V_{21}(t)$ given by Eqs. (6.3.6) and (6.3.7) we can insert them in Eq. (6.3.4). It is convenient to adopt several conventions at the same time. We will work with frequencies instead of energies, so we divide through by $\hbar$ and define

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} \tag{6.3.9}$$

$$\chi_{21} = e(\mathbf{r}_{21}\cdot\hat{\varepsilon})\frac{E_0}{\hbar} \tag{6.3.10a}$$

$$\chi_{12} = e(\mathbf{r}_{12}\cdot\hat{\varepsilon})\frac{E_0}{\hbar} \tag{6.3.10b}$$

Note that even though $\mathbf{r}_{12} = \mathbf{r}_{21}^*$ (see Problem 6.2), we cannot write $\chi_{12} = \chi_{21}^*$, since $\hat{\varepsilon}E_0$ may be complex (for circularly polarized radiation, for example). Evidently χ is the field–atom interaction energy in frequency units. It is also known as the "Rabi frequency," as we explain below. Also, we now set the arbitrary zero of energy at E_1, so $E_2 \to E_2 - E_1 = \hbar\omega_{21}$. Then Eqs. (6.3.4) become

$$i\dot{a}_1 = -\tfrac{1}{2}(\chi_{12}e^{-i\omega t} + \chi_{21}^* e^{i\omega t})\,a_2 \tag{6.3.11a}$$

$$i\dot{a}_2 = \omega_{21}a_2 - \tfrac{1}{2}(\chi_{21}e^{-i\omega t} + \chi_{12}^* e^{i\omega t})\,a_1 \tag{6.3.11b}$$

In the absence of any radiation field ($\chi = 0$) we find $a_1(t) = a_1(0)$ from (6.3.11a) and $a_2(t) = a_2(0)\exp[-i\omega_{21}t]$ from (6.3.11b). In the presence of a nearly resonant radiation field (6.3.1) oscillating at frequency $\omega \approx \omega_{21}$ we adopt similar trial solutions

$$a_1(t) = c_1(t) \tag{6.3.12a}$$

$$a_2(t) = c_2(t)\,e^{-i\omega t} \tag{6.3.12b}$$

and find these equations for $c_1(t)$ and $c_2(t)$:

$$i\dot{c}_1 = -\tfrac{1}{2}(\chi_{12}\,e^{-2i\omega t} + \chi_{21}^*)\,c_2 \tag{6.3.13a}$$

$$i\dot{c}_2 = (\omega_{21} - \omega)\,c_2 - \tfrac{1}{2}(\chi_{21} + \chi_{12}^* e^{2i\omega t})\,c_1 \tag{6.3.13b}$$

Equations (6.3.13) are more useful because of their isolation of the exp $[\pm 2i\omega t]$ terms. These terms oscillate so rapidly compared with every other time variation in the equations that they can be assumed to average to zero over any realistic time interval. In this way it is argued that they can simply be discarded. This is known as the *rotating-wave approximation* (abbreviated RWA in the optical resonance literature). It leads to these elementary working equations:

$$i\dot{c}_1 = -\tfrac{1}{2}\chi^* c_2 \tag{6.3.14a}$$

$$i\dot{c}_2 = \Delta c_2 - \tfrac{1}{2}\chi c_1 \tag{6.3.14b}$$

where we have dropped the subscript 21 from χ_{21} and have introduced Δ to stand for the atom–field frequency offset, or *detuning*:

$$\chi = \chi_{21} = (e\mathbf{r}_{21} \cdot \hat{\varepsilon})\frac{E_0}{\hbar} \tag{6.3.15a}$$

$$\Delta = \omega_{21} - \omega \tag{6.3.15b}$$

If $\hat{\varepsilon}E_0$ is a constant vector χ can be taken to be a purely real number. This can be arranged by the right choice of phases of the wave functions Φ_1 and Φ_2 (see Problem 6.3). Unless the context indicates otherwise (see Sec. 8.2), we will assume this has been done.

The great advantage of Eqs. (6.3.14) is their relative simplicity. The smallness of the coefficients Δ and χ (compared with ω and ω_{21}) shows that the c's are "slow" variables (compared with the a's). They contain the essential physics once the rapid oscillations associated with the frequencies ω and ω_{21} are removed by the rotating-wave approximation. The solutions for the c's are easily found (see Problem 6.4):

$$c_1(t) = \left(\cos\frac{\Omega t}{2} + i\frac{\Delta}{\Omega}\sin\frac{\Omega t}{2}\right)e^{-i\Delta t/2} \tag{6.3.16a}$$

$$c_2(t) = \left(i\frac{\chi}{\Omega}\sin\frac{\Omega t}{2}\right)e^{-i\Delta t/2} \tag{6.3.16b}$$

Here we have adopted the phase choice to make χ real. Also, we have assumed the atom to be in state 1 initially: $c_1(0) = 1$, $c_2(0) = 0$, and we have introduced the generalized Rabi frequency

$$\Omega = (\chi^2 + \Delta^2)^{1/2} \tag{6.3.17}$$

which reduces to the ordinary Rabi frequency χ at exact resonance ($\Delta = 0$). For this reason χ is sometimes called the resonance Rabi frequency.

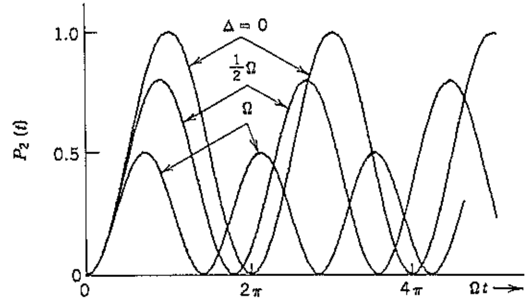

Figure 6.2 Plot of the upper-state probability $P_2(t)$ given by Eq. (6.3.18). Note that larger detuning Δ corresponds to higher frequency of Rabi oscillation but lower amplitude.

The corresponding probabilities $P_1(t) = |a_1(t)|^2$ and $P_2(t) = |a_2(t)|^2$ are

$$P_1(t) = \frac{1}{2}\left[1 + \left(\frac{\Delta}{\Omega}\right)^2\right] + \frac{1}{2}\left(\frac{\chi}{\Omega}\right)^2 \cos\Omega t \tag{6.3.18a}$$

$$P_2(t) = \frac{1}{2}\left(\frac{\chi}{\Omega}\right)^2 [1 - \cos\Omega t], \tag{6.3.18b}$$

The justification for defining Ω and χ exactly as we have and calling them (instead of $\Omega/2$ or 2Ω) "the" Rabi frequencies is evident in Figure 6.2, where $P_2(t)$ is plotted. It is clear that Ω is precisely the frequency at which probability oscillates between levels 1 and 2. It is easy to check that $P_1(t) + P_2(t) = 1$ for all t, so P_1 simply oscillates at the same frequency with the opposite phase from $P_2(t)$.

6.4 QUANTUM MECHANICS AND THE LORENTZ MODEL

In Chapters 2 and 3 we discussed Lorentz's classical electron oscillator model for the interaction of light with matter. Although this model is completely classical, it offers, as we saw, good explanations for a wide variety of phenomena. In this section we will explain, from the viewpoint of quantum mechanics, why the Lorentz model is so successful and also why the oscillator strength f must be introduced.

The basic dynamical variable for an atomic electron in the Lorentz model is its displacement $\mathbf{x}$. In order to establish the connection between the Lorentz model and the quantum-mechanical theory of an atomic electron, let us consider the corresponding quantum displacement, i.e., the expectation value $\langle \mathbf{r} \rangle$ in our two-state atom. By definition (5.2.20) this expectation value is

$$\langle \mathbf{r} \rangle = \int \Psi^*(\mathbf{r}, t)\, \mathbf{r}\, \Psi(\mathbf{r}, t)\, d^3r \tag{6.4.1}$$

For the two-state atom, $\Psi(\mathbf{r}, t)$ is given by the linear superposition (6.3.2) of the two stationary states. Thus

$$\begin{aligned} \langle \mathbf{r} \rangle &= \int (a_1^* \Phi_1^* + a_2^* \Phi_2^*)\, \mathbf{r}\, (a_1 \Phi_1 + a_2 \Phi_2)\, d^3r \\ &= |a_1|^2 \mathbf{r}_{11} + |a_2|^2 \mathbf{r}_{22} + a_1^* a_2 \mathbf{r}_{12} + a_2^* a_1 \mathbf{r}_{21} \end{aligned} \tag{6.4.2}$$

This complicated expression can be simplified. We noted in the preceding section that for atoms we can take $V_{11} = V_{22} = 0$, which means $\mathbf{r}_{11} = \mathbf{r}_{22} = 0$. Thus we have

$$\begin{aligned} \langle \mathbf{r} \rangle &= \mathbf{r}_{12} a_1^* a_2 + \mathbf{r}_{21} a_2^* a_1 \\ &= \mathbf{r}_{12} a_1^* a_2 + \text{c.c.} \end{aligned} \tag{6.4.3}$$

Since we are looking for a quantum analog to the Lorentzian physics of Chapters 2 and 3, we look for the equation of motion obeyed by the quantum expectation value $\langle \mathbf{r} \rangle$. For simplicity we consider linear polarization, so that $\hat{\varepsilon} E_0$ is real. From equations (6.3.4) we easily compute (retaining the choice of phases that leads to real-valued $\mathbf{r}_{21} \cdot \hat{\varepsilon} E_0$ and V_{21})

$$\hbar \frac{d}{dt}(a_1^* a_2) = -i(E_2 - E_1)\, a_1^* a_2 - iV_{21}\left(|a_1|^2 - |a_2|^2\right) \tag{6.4.4}$$

and

$$\begin{aligned} \hbar^2 \frac{d^2}{dt^2}(a_1^* a_2) = &-(E_2 - E_1)^2 a_1^* a_2 - (E_2 - E_1)\, V_{21}\left(|a_1|^2 - |a_2|^2\right) \\ &- i\hbar \frac{d}{dt}\left[V_{21}\left(|a_1|^2 - |a_2|^2\right)\right]. \end{aligned} \tag{6.4.5}$$

Therefore, since we have real $\mathbf{r}_{12}$ we can write

$$\langle \mathbf{r} \rangle = \mathbf{r}_{12}(a_1^* a_2 + a_1 a_2^*) \tag{6.4.6}$$

and we can combine (6.4.5) with its complex conjugate equation to get

$$\left(\frac{d^2}{dt^2} + \omega_0^2\right) \langle \mathbf{r} \rangle = +\frac{2e\omega_0}{\hbar} \mathbf{r}_{12}(\mathbf{r}_{21} \cdot \mathbf{E})\left(|a_1|^2 - |a_2|^2\right) \tag{6.4.7}$$

Here we have adopted the classical notation ω_0 for the transition frequency ω_{21}.

There is a close similarity of (6.4.7) to the Lorentz equation (2.2.18) for the classical electron displacement $\mathbf{x}$:

$$\left(\frac{d^2}{dt^2} + \omega_0^2\right) \mathbf{x} = \frac{e}{m} \mathbf{E} \tag{6.4.8}$$

To interpret the differences between (6.4.7) and (6.4.8) we first recall the special circumstances for which the Lorentz model was invented (around 1900). The phenomena Lorentz sought to explain involved only natural light (from the sun), or light from man-made thermal sources (lamps). The spectral intensity (W/cm^2-Hz) of any such radiation is weak (recall Section 1.2). This suggests that we focus our attention on the quantum equation (6.4.7) in the case in which the excited-state occupation probability is close to zero. [Sufficient conditions for this are worked out later, in Section 7.5.] In our two-state atom this means $|a_2|^2 \ll 1$ and therefore $|a_1|^2 \approx 1$, which gives

$$|a_1(t)|^2 - |a_2(t)|^2 \approx 1 \tag{6.4.9}$$

Under such circumstances of low excitation, we can approximate (6.4.7) by the equation

$$\left(\frac{d^2}{dt^2} + \omega_0^2\right) \langle \mathbf{r} \rangle = \frac{2e\omega_0}{\hbar} \mathbf{r}_{12}(\mathbf{r}_{21} \cdot \mathbf{E}) \tag{6.4.10}$$

This equation is still different from the Lorentz-model equation (6.4.8), but only in the constants on the right-hand side. Let us look at it more closely in a particular example.

Suppose the electric field points in the z direction ($\mathbf{E} = \hat{z}E$), so that

$$\left(\frac{d^2}{dt^2} + \omega_0^2\right) \langle \mathbf{r} \rangle = \frac{2e\omega_0}{\hbar} \mathbf{r}_{12} z_{21} E \tag{6.4.11}$$

and let the atomic states 1 and 2 be the 100 and 210 ($1s$ and $2p$) states of hydrogen. Then from Appendix 5.A we have

$$\Phi_1(\mathbf{r}) = R_{1,0}(r)\, Y_{0,0}(\theta, \phi) \tag{6.4.12}$$

$$\Phi_2(\mathbf{r}) = R_{2,1}(r)\, Y_{1,0}(\theta, \phi) \tag{6.4.13}$$

[This choice of states is discussed below. Spin does not play any role in this calculation. It may be assumed that $m_s = +\frac{1}{2}$ (or $-\frac{1}{2}$) for both states.] Now we can evaluate the three components of $\mathbf{r}_{12}$.

The components of $\mathbf{r}$ in Cartesian coordinates are shown in Figure 6.3 to be related to those in spherical coordinates by

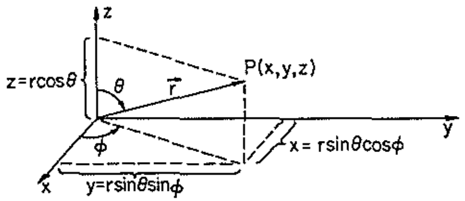

Figure 6.3 Cartesian components of the radius vector **r** in relation to spherical coordinates.

$$x = r \sin\theta \cos\phi \tag{6.4.14a}$$

$$y = r \sin\theta \sin\phi \tag{6.4.14b}$$

$$z = r \cos\theta \tag{6.4.14c}$$

We begin our evaluations with the z component:

$$\begin{aligned} z_{21} &= \int\!\!\int\!\!\int \Phi_2^*(\mathbf{r})\, z\Phi_1(\mathbf{r})\, d^3r \\ &= \int_0^\infty r^3 R_{2,1}^*(r)\, R_{1,0}(r)\, dr \int_0^{2\pi}\int_0^\pi Y_{1,0}^*(\theta,\phi) \sin\theta \cos\theta\, Y_{0,0}(\theta,\phi)\, d\theta\, d\phi \end{aligned} \tag{6.4.15}$$

The radial and angular integrations are traditionally considered separately. We consider the radial part first, and denote it r_{21}:

$$r_{21} = (2a_0^{-3/2}) \frac{2}{\sqrt{3}} (2a_0)^{-3/2} \int_0^\infty \left(\frac{r}{2a_0}\right) \exp\,(-r/2a_0)\, r^3 e^{-r/a_0}\, dr$$

With a change of variable and integral tables one finds

$$\int_0^\infty r^4 \exp\,(-3r/2a_0)\, dr = \left(\frac{2a_0}{3}\right)^5 \int_0^\infty x^4 e^{-x}\, dx = 4!\left(\frac{2a_0}{3}\right)^5$$

and therefore

$$r_{21} = 1.29a_0 \tag{6.4.16}$$

Note that we have verified the first line of Table 6.1 in Appendix 6.A. The angular part is also easily worked out. We will denote it by $\hat{z}_{21}$, where the circumflex indicates that the magnitude r has been taken out and we are considering the z component of the *unit vector* $\hat{\mathbf{r}} = \hat{\mathbf{x}} \sin\theta \cos\phi + \hat{\mathbf{y}} \sin\theta \sin\phi + \hat{\mathbf{z}} \cos\theta$. We find the value

$$\begin{aligned} \hat{z}_{21} &= \sqrt{\frac{1}{4\pi}\frac{3}{4\pi}} \int_0^{2\pi} d\phi \int_0^\pi \cos^2\theta \sin\theta\, d\theta \\ &= \frac{\sqrt{3}}{4\pi} 2\pi \int_{-1}^{1} x^2\, dx \\ &= \sqrt{\tfrac{1}{3}} \end{aligned} \tag{6.4.17}$$

The combination of (6.4.16) and (6.4.17) then gives

$$z_{21} = r_{21}\hat{z}_{21} = 0.745a_0 \tag{6.4.18}$$

Proceeding in exactly the same fashion, we find that x_{21} and y_{21} vanish for the states (6.4.12) and (6.4.13). It is easy to see why: x and y have ϕ dependences of $\cos\phi$ and $\sin\phi$, respectively. Since the integral from 0 to 2π of either $\cos\phi$ or $\sin\phi$ is zero, $x_{21} = y_{21} = 0$. Note that we have verified the first line of Table 6.2 in Appendix 6.A.

Equation (6.4.11) may therefore be simplified:

$$\left(\frac{d^2}{dt^2} + \omega_0^2\right)\langle \mathbf{r} \rangle = \frac{2e\omega_0}{\hbar}\, \hat{\mathbf{z}} z_{12} z_{21} E \tag{6.4.19}$$

$$= \frac{2e\omega_0}{\hbar} (z_{12})^2 \mathbf{E} \tag{6.4.20}$$

Now we observe that if in the classical formula (6.4.8) we make the replacement

$$\frac{e}{m} \to \frac{2e\omega_0}{\hbar} z_{12}^2 \tag{6.4.21}$$

or equivalently

$$\begin{aligned} \frac{e^2}{m} &\to \frac{2e^2\omega_0}{\hbar} z_{12}^2 \\ &= \frac{e^2}{m}\left[\frac{2m\omega_0}{\hbar} z_{12}^2\right] \end{aligned} \tag{6.4.22}$$

then *Lorentz's classical equation for* **x** *is exactly the same as the quantum-mechanical equation for* $\langle \mathbf{r} \rangle$ *under the ground-state approximation* (6.4.9).

Comparing (6.4.22) with (3.7.5), it is evident that they agree if we identify the factor in brackets in the former with the oscillator strength factor f:

$$f = \frac{2m\omega_0}{\hbar} z_{12}^2$$

Since f values have been known from absorption and dispersion experiments for many years, this identification can easily be tested. Using our calculated result (6.4.18) and the expression $\omega_0 = (E_2 - E_1)/\hbar$ for the Bohr transition frequency, we compute from (6.4.22) the (dimensionless) numerical value

$$f = 0.416 \tag{6.4.23}$$

Comparison with the first entry of Table 3.1 confirms that 0.416 is indeed the oscillator strength of the $n = 1 \rightarrow n = 2$ transition of hydrogen. This shows that we have not only demonstrated the validity in quantum theory of the Lorentz model under conditions of low excitation ($|a_2|^2 \ll 1$), but we have also derived an expression for the oscillator strength of the transition in terms of fundamental atomic parameters. We note that the presence of $\hbar$ indicates the quantum nature of f.

Our example gives the impression that the z direction plays a special role. This is not actually the case. We can correct the misimpression as follows. First we note that the classical atom, according to (6.4.8), is free to respond to the electric field, no matter in what direction **E** points. On the other hand, according to (6.4.10) the quantum mechanical atom responds only to the component of the field parallel to the matrix element vector $\mathbf{r}_{21}$. That is, the quantum mechanical atom appears to have an internal or intrinsic sense of direction.

In fact a quantum mechanical atom does have a sense of direction if it is exposed to orienting or aligning forces such as from static external electric or magnetic fields. External forces have the effect of destroying ("lifting") the degeneracy of states mentioned in Section 4.3. When the degeneracy is lifted, each set (n, l, m) of state quantum numbers refers to a distinct value of energy. Conversely, in the absence of external alignment or orientation (in an atom in free space) each transition is degenerate since all possible m's associated with the same l denote states with the same energy. Thus, to compare a quantum mechanical atom with a classical atom in free space requires that the degeneracy of the initial and final states be recognized. Figure 6.4 shows the states with differing m values contributing to the $1s$–$2p$ transition chosen in (6.4.12) and (6.4.13) above. Figure 6.5 shows the corresponding situation for a p–d transition.

We see now that the right-hand side of (6.4.10) correctly refers to an atom in free space only if the three possible m values ($+1$, 0, -1) of the $2p$ state are all included. As it happens, for an $s \rightarrow p$ transition, if the field is polarized in the z direction as assumed in the calculation, the $m = \pm 1$ contributions to the result turn out to be zero [see Problem 6.6a]. This is why the calculation reached the correct result, given in (6.4.23).

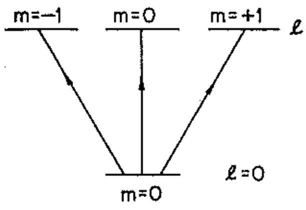

Figure 6.4 Absorptive transitions between an s level ($l = 0$) and a p level ($l = 1$). The transition $m = 0 \rightarrow 0$ occurs in a linearly polarized field, whereas the $m = 0 \rightarrow +1$ and $m = 0 \rightarrow -1$ transitions occur in left and right circularly polarized fields, respectively.

On the other hand, if the field had not been chosen in the z direction, then the $m = \pm 1$ terms would have contributed enough to the result to produce the same final number. This follows from the important quantum mechanical result

$$\textstyle\sum_{m\text{'s}} |x_{12}|^2 = \sum_{m\text{'s}} |y_{12}|^2 = \sum_{m\text{'s}} |z_{12}|^2 \tag{6.4.24}$$

where the summations are over all of the m values for levels 1 and 2. The usual expression for the oscillator strength f recognizes these and other symmetry principles [see Problem 6.8]. As a result f is conventionally written in terms of the isotropic combination $|x_{12}|^2 + |y_{12}|^2 + |z_{12}|^2 = \mathbf{r}_{12}\cdot\mathbf{r}_{21}$, as follows:

$$f = (2m\omega_{21}/3\hbar) \textstyle\sum_m \mathbf{r}_{12}\cdot\mathbf{r}_{21} \tag{6.4.25}$$

where the sum is over the m values of the *final* state of the transition. Note that the final state is unambiguously Φ_2 in our example because of our assumption about level probabilities in (6.4.9).

This quantum-mechanical validation of the classical Lorentz model is little short of wonderful. We have shown that, under conditions of low excitation probability, an atomic electron responds to an electric field exactly as if it were bound by a spring to the nucleus. The classical oscillation frequency ω_0 corresponds to a Bohr transition frequency, just as we surmised in Chapters 2 and 3. And if we want the

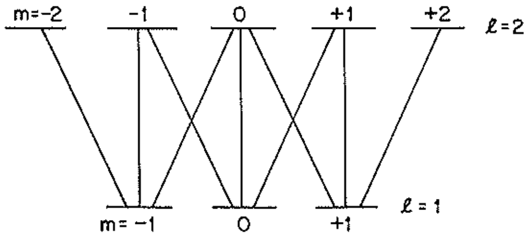

Figure 6.5 Transitions between p and d levels.

classical Lorentz model to agree in quantitative detail with quantum mechanics, we simply introduce the oscillator strength as in (3.7.5).

We have now justified the Lorentz model quantum-mechanically in a special case, but have included only two atomic levels in our calculations. It is not difficult to justify the Lorentz model using the full time-dependent Schrödinger equation (6.2.8) for the probability amplitudes of *all* atomic levels, assuming that the atom remains with high probability in the ground level. Actually, however, it is usually not really essential, under conditions of low excitation probability, to include more than the ground and first excited levels of an atom. The reason for this is made clear by inspection of Table 3.1 for the oscillator strengths of hydrogen: the transition involving the $n = 1$ and $n = 2$ energy levels has a much larger oscillator strength than other transitions involving the ground level. Thus our two-level approach, including only $n = 1$ and $n = 2$ levels, is a reasonable approximation under conditions of high ground-state probability.

6.5 DENSITY MATRIX AND COLLISIONAL RELAXATION

The identification of quantum and classical electron displacements $\langle \mathbf{r} \rangle$ and $\mathbf{x}$ allows the classical Lorentz theory to be put in its correct perspective, as we showed in the preceding section. The same identification assists us with our development of the quantum theory of absorption and emission, because it correctly suggests, via Eq. (6.4.3), that the combinations $a_1^* a_2$ and $a_1 a_2^*$ are more useful than either a_1 or a_2 alone.

We will pursue this approach by obtaining the equations of motion for these combination variables, except that we will focus on the related but simpler quantities c_1 and c_2 defined in (6.3.12). First we adopt a conventional notation and use the Greek letter ρ (rho) to define

$$\rho_{12} \equiv c_1 c_2^* \tag{6.5.1a}$$

$$\rho_{21} \equiv c_2 c_1^* \tag{6.5.1b}$$

$$\rho_{11} \equiv c_1 c_1^* = |c_1|^2 \tag{6.5.1c}$$

$$\rho_{22} \equiv c_2 c_2^* = |c_2|^2 \tag{6.5.1d}$$

The ρ's are elements of the so-called "density matrix" of the atom, as we explain briefly at the end of this section. However, independent of this terminology, it is clear that ρ_{11} and ρ_{22} are just new ways to write the levels' occupation probabilities. The physical meanings of ρ_{12} and ρ_{21} are related to the electron displacement vector through (6.4.3) and (6.3.12), so we can think of ρ_{21} as the complex amplitude of the electron's displacement $\langle \mathbf{r} \rangle$.

By using equations (6.3.14) repeatedly we can easily derive the following equations for the ρ's (see Problem 6.9):

$$\dot{\rho}_{12} = i\Delta\rho_{12} + i\frac{\chi^*}{2}(\rho_{22} - \rho_{11}) \tag{6.5.2a}$$

$$\dot{\rho}_{21} = -i\Delta\rho_{21} - i\frac{\chi}{2}(\rho_{22} - \rho_{11}) \tag{6.5.2b}$$

$$\dot{\rho}_{11} = -\frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21}) \tag{6.5.2c}$$

$$\dot{\rho}_{22} = \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21}) \tag{6.5.2d}$$

The solutions of these equations can be constructed from the solutions for $c_1(t)$ and $c_2(t)$ given in (6.3.16).

However, the equations themselves are not yet in their most useful form. This is because they do not reflect the existence of relaxation processes such as collisions. The same statistical principles employed to treat collisions in Chapter 3 will be used again here. There will be one added complication compared with the classical case, originating with the population variables ρ_{22} and ρ_{11}, which have no classical counterparts.

First we will concentrate on the electron's complex displacement variable ρ_{21}, and on one type of collision, namely purely elastic collisions, which do not affect the populations ρ_{11} and ρ_{22}. If the radiation field present is steady, then $\chi =$ constant. We require the solution for $\rho_{21}(t)$ that vanishes at an earlier time t_1, which (as in Chapter 3) we associate with the time of the atom's most recent collision. We assume that collisions are frequent, so that $t - t_1$ is short enough to neglect changes in $\rho_{22} - \rho_{11}$. The required solution is:

$$\rho_{21}(t)\big|_{t_1} = -\frac{\chi(\rho_{22} - \rho_{11})}{2\Delta}\left(1 - e^{-i\Delta(t-t_1)}\right). \tag{6.5.3}$$

This can be checked by substitution in (6.5.2b), remembering to hold χ and $\rho_{22} - \rho_{11}$ constant. Next we average this solution over all possible earlier times t_1 at which a collision might have occurred, using the familiar expression (3.9.4) for the probability df that the collision occurred in the time between t_1 and $t_1 + dt_1$:

$$df(t, t_1) = e^{-(t-t_1)/\tau}\frac{dt_1}{\tau} \tag{6.5.4}$$

The result is

$$\begin{aligned} \langle \rho_{21}(t) \rangle &= -\frac{\chi(\rho_{22} - \rho_{11})}{2\Delta\tau}\int_{-\infty}^{t} dt_1\, e^{-(t-t_1)/\tau}\left(1 - e^{-i\Delta(t-t_1)}\right) \\ &= -\frac{\chi(\rho_{22} - \rho_{11})}{2}\,\frac{1}{\Delta - i/\tau} \end{aligned} \tag{6.5.5}$$

• It is instructive to compare (6.5.5) in detail with its classical counterpart, which is (3.9.7). Since $\langle \mathbf{x} \rangle$ was written there in complex form, the correspondence is $\langle \mathbf{x} \rangle_{\text{cl}} \to \langle \mathbf{r} \rangle_{\text{qm}} = 2\mathbf{r}_{12} \langle \rho_{21} \rangle e^{-i(\omega t - kz)}$. As we have seen above, we should also take $\rho_{22} \to 0$ and $\rho_{11} \to 1$ for a classical comparison. Furthermore the equations for c_1 and c_2, and thus for ρ_{21}, were written in the rotating-wave approximation, which assumes the near-resonance condition $\omega_0 \approx \omega$, or $\omega_0^2 - \omega^2 \approx 2\omega(\omega_0 - \omega) = 2\omega\Delta$. With these adjustments, to ensure similarity of assumptions, we find

$$\langle \mathbf{x} \rangle_{\text{cl}} \to \frac{e}{2m\omega} \frac{\hat{\boldsymbol{\varepsilon}} E_0 \, e^{-i(\omega t - kz)}}{\Delta - i/\tau + 1/2\omega\tau^2} \tag{6.5.6}$$

$$\langle \mathbf{r} \rangle_{\text{qm}} \to \frac{e\mathbf{r}_{12}(\mathbf{r}_{21} \cdot \hat{\boldsymbol{\varepsilon}})}{\hbar} \frac{E_0 \, e^{-i(\omega t - kz)}}{\Delta - i/\tau} \tag{6.5.7}$$

We can drop the final term in the denominator of (6.5.6) because it has already been discarded in Chapter 3. If we replace ω by ω_{21}, as the resonance approximation permits, then the only other difference between the classical and quantum expressions is the difference between $(e/2m\omega_{21})\hat{\boldsymbol{\varepsilon}}$ and $e\mathbf{r}_{12}(\mathbf{r}_{21} \cdot \hat{\boldsymbol{\varepsilon}})/\hbar$, which we determined in Section 6.4 to be just a factor of *f*, the oscillator strength. Thus the quantum and classical theories are again found to be in complete accord, given the universal use of the oscillator-strength factor in classical formulas—again, *if* we put all of the atomic population in the ground level, $\rho_{22} - \rho_{11} = -1$. •

The same result (6.5.5), obtained by a collision average, can also be reached by a simple modification of the original equation of motion. It can be checked (Problem 6.10) that collisions are already included if we rewrite the ρ_{21} and ρ_{12} equations as follows:

$$\dot{\rho}_{12} = -\left(\frac{1}{\tau} - i\Delta\right)\rho_{12} + i\frac{\chi^*}{2}(\rho_{22} - \rho_{11}) \tag{6.5.8a}$$

$$\dot{\rho}_{21} = -\left(\frac{1}{\tau} + i\Delta\right)\rho_{21} - i\frac{\chi}{2}(\rho_{22} - \rho_{11}) \tag{6.5.8b}$$

As in the classical case, we cannot apply these equations any longer to an individual atom. Instead they represent an "average" atom in the sense of the collision average in (6.5.5). We have omitted averaging brackets $\langle \cdots \rangle$ for notational convenience, as in the classical discussion.

Note that equations (6.5.8) can be read as if the average atom's ρ_{12} and ρ_{21} variables undergo change for two reasons. That is, we can interpret (6.5.8b) as the result of adding two independent rates of change:

$$\rho_{21} = (\dot{\rho}_{21})_{\text{elastic collisions}} + (\dot{\rho}_{21})_{\text{Schrödinger equation}} \tag{6.5.9}$$

where

$$(\dot{\rho}_{21})_{\text{elastic collisions}} = -\frac{1}{\tau}\rho_{21} \tag{6.5.10a}$$

and

$$(\dot{\rho}_{21})_{\text{Schrödinger equation}} = -i\Delta\rho_{21} - i\frac{\chi}{2}(\rho_{22} - \rho_{11}) \tag{6.5.10b}$$

Such an interpretation will be very helpful in dealing with the effect of collisions on the level populations ρ_{22} and ρ_{11}, for which there are no classical analogs.

The collision rate $1/\tau$ appearing in (6.5.8) is often referred to as the atomic dipole's "dephasing" rate. To understand this we can recall the discussion in Section 3.9, following Eq. (3.9.12). It was assumed there that the orientation of both $\mathbf{x}$ and $d\mathbf{x}/dt$ was random for each dipole after a collision, and thus zero on average. No assumption was made about $(\mathbf{x})^2$ or $(d\mathbf{x}/dt)^2$. That is, both classically and quantum-mechanically we have been discussing only the effects of energy-nonchanging (elastic) collisions. However, inelastic collisions can also occur, in which the electron can change its energy level.

To account for inelastic collisions we simply assert that their effect is to knock population out of levels 1 and 2 into other unspecified levels of the atom at the fixed rates Γ_1 and Γ_2. At the same time we can include the effect of spontaneous photon emission as a special type of "collision" that transfers population between the two specified levels, from 2 to 1. Following Einstein's notation we will denote the spontaneous emission rate by A_{21}. Then we write, in analogy to (6.5.9),

$$\dot{\rho}_{22} = (\dot{\rho}_{22})_{\text{collisions}} + (\dot{\rho}_{22})_{\text{spontaneous emission}} + (\dot{\rho}_{22})_{\text{Schrödinger equation}} \tag{6.5.11}$$

where

$$(\dot{\rho}_{22})_{\text{collisions}} = -\Gamma_2\rho_{22} \tag{6.5.12a}$$

$$(\dot{\rho}_{22})_{\text{spontaneous emission}} = -A_{21}\rho_{22} \tag{6.5.12b}$$

$$(\dot{\rho}_{22})_{\text{Schrödinger equation}} = \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21}) \tag{6.5.12c}$$

In a similar vein we write the separate contributions to $\dot{\rho}_{11}$:

$$(\dot{\rho}_{11})_{\text{collisions}} = -\Gamma_1\rho_{11} \tag{6.5.13a}$$

$$(\dot{\rho}_{11})_{\text{spontaneous emission}} = +A_{21}\rho_{22} \tag{6.5.13b}$$

$$(\dot{\rho}_{11})_{\text{Schrödinger equation}} = -\frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21}) \tag{6.5.13c}$$

Note that the contribution from spontaneous emission to $\dot{\rho}_{11}$ is positive, and just equal to the negative contribution to $\dot{\rho}_{22}$, on the assumption that the atom makes a jump from level 2 to level 1 while emitting a photon spontaneously.

As a result of these collisional and spontaneous contributions we obtain the following equations for the level populations:

$$\dot{\rho}_{11} = -\Gamma_1\rho_{11} + A_{21}\rho_{22} - \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21}) \qquad (6.5.14a)$$

$$\dot{\rho}_{22} = -(\Gamma_2 + A_{21})\rho_{22} + \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21}) \qquad (6.5.14b)$$

Again, for notational convenience, we do not include brackets $\langle \cdots \rangle$. However, these equations must also be understood as applying only in an average sense to the atoms under consideration.

Finally we must return to the elastic-collision-averaged ρ_{12} and ρ_{21} equations. What is the effect of inelastic collisions on them? A simple answer is based on the obvious relation $|\rho_{12}| = (\rho_{11}\rho_{22})^{1/2}$, which holds before collision averaging. It is a direct consequence of the definitions (6.5.1). This relation says that the effect of collisions on the *magnitude* of ρ_{12}, as distinct from the effect on its *phase*, is directly related to the effect on the level populations in a specific way. That is, if inelastic collisions alone cause ρ_{11} and ρ_{22} to decay, i.e.,

$$\rho_{11}(t)\big|_{\text{collisions}} = \rho_{11}(0)\,e^{-\Gamma_1 t} \qquad (6.5.15a)$$

$$\rho_{22}(t)\big|_{\text{collisions}} = \rho_{22}(0)\,e^{-\Gamma_2 t} \qquad (6.5.15b)$$

which are the solutions to (6.5.12a) and (6.5.13a), then inelastic collisions alone cause $|\rho_{12}(t)|$ to decay as

$$\begin{aligned}|\rho_{12}(t)| &= [\rho_{11}(t)\,\rho_{22}(t)]^{1/2}\\ &= [\rho_{11}(0)\,\rho_{22}(0)\exp[-(\Gamma_1 + \Gamma_2)t]]^{1/2}\\ &= |\rho_{12}(0)|\exp\left(-\frac{\Gamma_1 + \Gamma_2}{2}t\right) \qquad (6.5.16)\end{aligned}$$

In words, the effect on ρ_{12} of inelastic collisions alone is to add an extra decay rate to the elastic collision decay rate $1/\tau$. This added rate is just $(\Gamma_1 + \Gamma_2)/2$, one-half the sum of the population decay rates for ρ_{11} and ρ_{22}.

Thus we write our final equations for ρ_{12} and ρ_{21} averaged over both elastic and inelastic collisions (and including spontaneous emission) in the form

$$\dot{\rho}_{12} = -(\beta - i\Delta)\rho_{12} + i\frac{\chi^*}{2}(\rho_{22} - \rho_{11}) \qquad (6.5.17a)$$

$$\dot{\rho}_{21} = -(\beta + i\Delta)\rho_{21} - i\frac{\chi}{2}(\rho_{22} - \rho_{11}) \qquad (6.5.17b)$$

where β is the total relaxation rate:

$$\beta = \frac{1}{\tau} + \tfrac{1}{2}(\Gamma_1 + \Gamma_2 + A_{21}) \qquad (6.5.18)$$

Only the first term in β refers to elastic ("soft" or "dephasing") collisions, but it is often dominant. It is usually likely that an atom suffers many distant soft dephasing collisions for every close collision that is hard enough to cause population changes. Thus, to a good approximation in many cases

$$\beta \approx \frac{1}{\tau} \gg \tfrac{1}{2}(\Gamma_1 + \Gamma_2 + A_{21}) \qquad (6.5.19)$$

To a surprising degree, laser action of the usual kind depends very strongly on this inequality. We will require (6.5.19) in the next chapter.

The effects of collisional dephasing relaxation can be illustrated in detail by integrating the coupled equations for the ρ's (see Problem 6.11). In Figure 6.6 we show the solutions for a wide range of parameters. We have chosen a special case that is free of complications. We take $\Gamma_1 = \Gamma_2 = 0$ (no transfer of probability to levels other than 1 and 2), and we take $\Delta = 0$ (exact resonance). Since $\Gamma_1 = \Gamma_2 = 0$, we have $d\rho_{11}/dt + d\rho_{22}/dt = 0$. Thus, $\rho_{11} + \rho_{22} = 1$ (conservation of probability), and it is enough to determine either ρ_{11} or ρ_{22}. Actually it is most convenient to deal with the inversion $\rho_{22} - \rho_{11}$, since it enters Eqs. (6.5.17) naturally. Furthermore, Eqs. (6.5.17) show that at exact resonance $\rho_{21} + \rho_{12}$ is coupled only to itself and plays no role in the dynamics, so we can pay attention solely to the difference, $\rho_{12} - \rho_{21}$, which in any event is the variable that couples directly to ρ_{11} and ρ_{22}, as Eqs. (6.5.14) make clear.

Thus we can focus on two real variables

$$v = i(\rho_{21} - \rho_{12}) \qquad (6.5.20a)$$

$$w = \rho_{22} - \rho_{11} \qquad (6.5.20b)$$

which obey the equations (at resonance, and in the absence of the Γ_1 and Γ_2 collisions and for real χ)

$$\dot{v} = -\beta v + \chi w \qquad (6.5.21a)$$

$$\dot{w} = -A_{21}(1 + w) - \chi v \qquad (6.5.21b)$$

These equations can be obtained directly from (6.5.14) and (6.5.17) and the definitions in (6.5.20). They are discussed further in Chapter 8. Of course, following (6.5.18) and the absence of Γ_1 and Γ_2, we have $\beta = 1/\tau + A_{21}/2$.

The solutions shown in Figure 6.6 are chosen to illustrate the influence of elastic

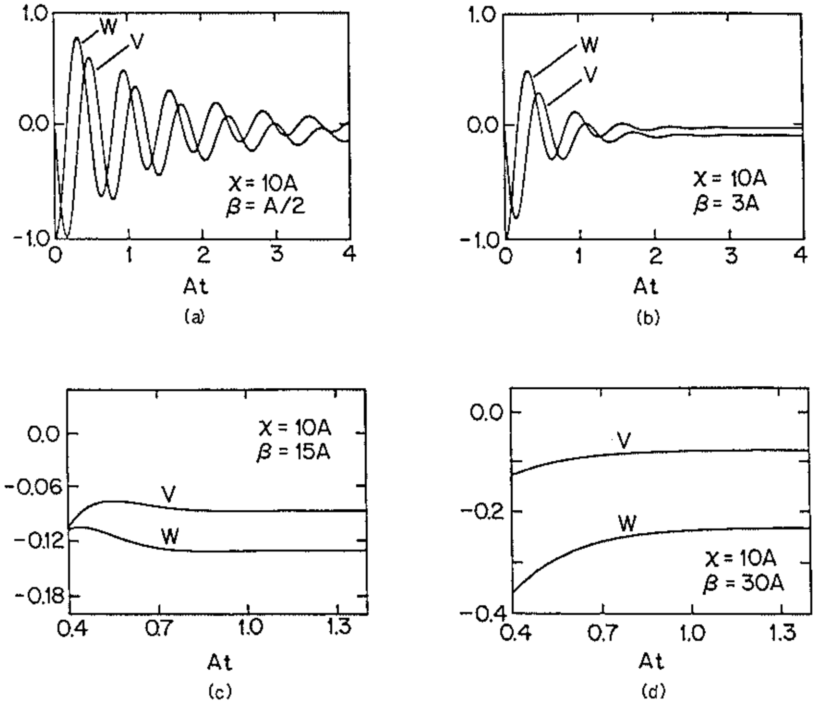

Figure 6.6 Numerical solutions of the v, w equations (6.5.21) for a range of collisional damping rates. Note scale changes.

collisions. As the elastic-collision rate $1/\tau$ increases from zero, the damping parameter β also increases and the oscillatory (so-called "coherent") response of the atom to the applied radiation changes to nonoscillatory ("incoherent") decay. Note the changes in scale needed in the figure to make evident the different types of response.

• The notation used for the ρ's suggests that they are the elements of a 2×2 matrix:

$$\underline{\rho} = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \tag{6.5.22}$$

This is indeed the case, and quantum statistical mechanics is devoted to the study of such matrices. They were introduced into quantum theory independently by L. D. Landau and J. von Neumann before 1930. For historical reasons $\underline{\rho}$ is called the *density matrix* of the system, and in this case $\underline{\rho}$ is the density matrix of a two-level atom.

The density matrix is a generalization of a related 2×2 matrix

$$\begin{bmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{bmatrix} \tag{6.5.23}$$

and the two are occasionally confused. Note that they are *not* the same matrix, despite the original definitions in (6.5.1): $\rho_{11} = c_1 c_1^*$, $\rho_{12} = c_1 c_2^*$, etc. This is because the ρ's are now understood to refer to collision averages of $c_1 c_1^*$, etc. Thus the equations (6.5.14) and (6.5.17) for the elements of the density matrix cannot be obtained from simpler equations for c_1 and c_2 separately. [The reader is challenged to try to construct equations for c_1 and c_2 that can be used to obtain (6.5.14) and (6.5.17).] This is the most important sense in which the cc^* combinations are more physical than c's and c^*'s alone.

The existence of the matrix (6.5.22) establishes a definite meaning to the terms "diagonal" and "off-diagonal". Obviously ρ_{11} and ρ_{22} are the elements on the diagonal, and ρ_{12} and ρ_{21} are the off-diagonal elements. This terminology is frequently applied to the damping rates. Referring to Eqs. (6.5.14), we see that Γ_1 and $\Gamma_2 + A_{21}$ can be called diagonal damping rates, and from Eqs. (6.5.17) we see that β is the off-diagonal damping rate. A fundamental relation, obtained from (6.5.18), is illustrated by the inequality

$$\beta \geq \tfrac{1}{2}(\Gamma_1 + \Gamma_2 + A_{21}) \tag{6.5.24}$$

As we have seen, because the off-diagonal elements ρ_{12} and ρ_{21} have a complex phase as well as a magnitude, they are susceptible to purely phase-destructive, as well as population-changing, relaxation. •

APPENDIX 6.A MATRIX ELEMENTS OF THE ELECTRON COORDINATE r FOR LOW-LYING STATES OF HYDROGEN

The coordinate vector $\mathbf{r}$ can be written $\mathbf{r} = r\hat{\mathbf{r}}$, where $r = |\mathbf{r}|$ is the magnitude of $\mathbf{r}$, and $\hat{\mathbf{r}} = \hat{\mathbf{x}} \sin\theta \cos\phi + \hat{\mathbf{y}} \sin\theta \sin\phi + \hat{\mathbf{z}} \cos\theta$ is the radial unit vector (recall Figure 6.3). The matrix element of $\mathbf{r}$ between two states Φ_1 and Φ_2 is defined by (6.3.8):

$$\mathbf{r}_{12} = \iiint \Phi_1^*(\mathbf{r})\,\mathbf{r}\,\Phi_2(\mathbf{r})\,d^3r \tag{6.A.1}$$

We separate the integral into its radial and angular parts, according to the corresponding separation of the wave functions of Appendix 5.A. That is,

$$\mathbf{r}_{12} = r_{12}\hat{\mathbf{r}}_{12} \tag{6.A.2}$$

where r_{12} is the matrix element of r, and $\hat{\mathbf{r}}_{12}$ is the matrix element of the radial unit vector $\hat{\mathbf{r}}$. In terms of hydrogen wave functions we have

TABLE 6.1 Radial Coordinate Matrix Elements for Atomic Hydrogen

Transition	r_{12}/a_0	r_{12}^2/a_0^2
1*s*–2*p*	1.29	1.66
1*s*–3*p*	0.517	0.267
1*s*–4*p*	0.305	0.093
2*s*–3*p*	3.07	9.4
2*s*–4*p*	1.28	1.64
2*p*–3*s*	0.95	0.9
2*p*–3*d*	4.75	22.5
2*p*–4*d*	1.71	2.92

TABLE 6.2 Cartesian Components of Angular Matrix Elements

Angular Matrix Element	*x* Component	*y* Component	*z* Component
…… *s*–*p* Transitions ……			
$(00\vert\hat{\mathbf{r}}\vert 10)$	0	0	$\sqrt{\frac{1}{3}}$
$(00\vert\hat{\mathbf{r}}\vert 11)$	$-\sqrt{\frac{1}{6}}$	$-i\sqrt{\frac{1}{6}}$	0
$(00\vert\hat{\mathbf{r}}\vert 1\ -1)$	$\sqrt{\frac{1}{6}}$	$-i\sqrt{\frac{1}{6}}$	0
…… *p*–*d* Transitions ……			
$(10\vert\hat{\mathbf{r}}\vert 20)$	0	0	$\sqrt{\frac{4}{15}}$
$(10\vert\hat{\mathbf{r}}\vert 21)$	$-\sqrt{\frac{1}{10}}$	$-i\sqrt{\frac{1}{10}}$	0
$(10\vert\hat{\mathbf{r}}\vert 2\ -1)$	$\sqrt{\frac{1}{10}}$	$-i\sqrt{\frac{1}{10}}$	0
$(10\vert\hat{\mathbf{r}}\vert 22)$	0	0	0
$(10\vert\hat{\mathbf{r}}\vert 2\ -2)$	0	0	0
$(11\vert\hat{\mathbf{r}}\vert 20)$	$\sqrt{\frac{1}{30}}$	$-i\sqrt{\frac{1}{30}}$	0
$(11\vert\hat{\mathbf{r}}\vert 21)$	0	0	$\sqrt{\frac{1}{5}}$
$(11\vert\hat{\mathbf{r}}\vert 2\ -1)$	0	0	0
$(11\vert\hat{\mathbf{r}}\vert 22)$	$-\sqrt{\frac{1}{5}}$	$-i\sqrt{\frac{1}{5}}$	0
$(11\vert\hat{\mathbf{r}}\vert 2\ -2)$	0	0	0
$(1\ -1)\vert\hat{\mathbf{r}}\vert 20)$	$-\sqrt{\frac{1}{30}}$	$-i\sqrt{\frac{1}{30}}$	0
$(1\ -1)\vert\hat{\mathbf{r}}\vert 21)$	0	0	0
$(1\ -1)\vert\hat{\mathbf{r}}\vert 2\ -1)$	0	0	$\sqrt{\frac{1}{5}}$
$(1\ -1)\vert\hat{\mathbf{r}}\vert 22)$	0	0	0
$(1\ -1)\vert\hat{\mathbf{r}}\vert 2\ -2)$	$\sqrt{\frac{1}{5}}$	$-i\sqrt{\frac{1}{5}}$	0

$$r_{12} = \int R^*_{n_1 l_1}(r)\, r R_{n_2 l_2}(r)\, r^2\, dr \tag{6.A.3}$$

$$\hat{\mathbf{r}}_{12} = \iint Y^*_{l_1 m_1}(\theta, \phi)\, \hat{\mathbf{r}}\, Y_{l_2 m_2}(\theta, \phi) \sin\theta\, d\theta\, d\phi \tag{6.A.4}$$

The radial part depends only on principal quantum numbers and orbital angular momenta (n, l), and we find the values in Table 6.1. For the vector part of $\mathbf{r}_{12}$ we use the notation

$$\hat{\mathbf{r}}_{12} = (l_1 m_1 | \hat{\mathbf{r}} | l_2 m_2) \tag{6.A.5}$$

and we give the Cartesian components of the matrix element separately in Table 6.2.

PROBLEMS

6.1 Show that the factorization (5.3.4) does not work when H is time-dependent. That is, show that the resulting equation for $\Phi(\mathbf{r})$ depends on t, and so $\Phi(\mathbf{r})$ itself must depend on t, contrary to the factorization assumption.

6.2 From the definition of $\mathbf{r}_{12}$ in (6.3.8), show that $(\mathbf{r}_{12})^* = \mathbf{r}_{21}$.

6.3 Every solution $\Phi(\mathbf{r})$ of the Schrödinger equation (5.4.1) remains a solution when multiplied by a constant K, and it remains normalized according to (5.4.6) if K is a pure phasor: $K = e^{i\mu}$. In this sense every $\Phi(\mathbf{r})$ has arbitrary complex phase that can be adjusted for convenience. Assume that an initial phase choice for the wave functions Φ_1 and Φ_2 (perhaps from a table such as given in Appendix 5.A) leads to the complex matrix element $V_{12} = \alpha - i\beta$ (where α and β are real).

(a) Replace Φ_1 by $K\,\Phi_1$. Find the value of K that makes V_{12} real.

(b) What is the new purely real value of V_{12}?

6.4 (a) Find the second-order differential equations satisfied by the probability amplitudes c_1 and c_2 by differentiation and substitution between Eqs. (6.3.14).

(b) Write the general solution for $c_2(t)$ in terms of $\sin(\Omega t/2)$ and $\cos(\Omega t/2)$, and fix the coefficients to fit the initial condition $c_1(0) = 0$, $c_2(0) = 1$.

(c) The initial condition specified in (b) is opposite to the one used to obtain the solutions (6.3.16) in the text. Comment on the differences (if any) between (6.3.16) and the solutions obtained in (b).

6.5 Use the definition of $\mathbf{r}_{12}$ in (6.3.8) to show that $\mathbf{r}_{11} = 0$. To obtain this result you must assume that $|\Phi_1(\mathbf{r})|^2$ is an even function of $\mathbf{r}$. More precisely, $\Phi_1(\mathbf{r})$ must have a definite *parity*, i.e., $\Phi_1(-\mathbf{r})$ is identically the same as either $\Phi_1(\mathbf{r})$ (even parity) or $-\Phi_1(\mathbf{r})$ (odd parity).