

INTERACTION OF A QUANTUM SYSTEM
WITH A STRONG OSCILLATING FIELD

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ABSTRACT

The problem of the interaction of a quantum system having discrete states, with a classical oscillating field, is reexamined as a problem in the solution of the time-dependent Schrödinger equation with a periodic Hamiltonian. A method is presented for approximating the time-dependent Hamiltonian with a time-independent one in the weak oscillating field case. With the aid of Floquet's theorem the problem is exactly converted to one with a time-independent Hamiltonian represented by an infinite matrix. The approximation of only two states then permits finding the resonance line shape by perturbation theory for both single and multiple quantum transitions with equal ease. The simple case of only two states connected by an off diagonal sinusoidal perturbation is studied in detail, and a complete description of the average transition probability is found for the strong oscillating field case. A few more complex cases are discussed. A deeper understanding of the analysis is obtained by examining the theory with the oscillating field quantized. Experimental verification of the theory could best be obtained by the methods of atomic beam spectroscopy at radio frequencies.

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I. INTRODUCTION

Early in the development of quantum mechanics, Dirac provided an approximate treatment of the interaction of an atom with the electromagnetic field. This theory adequately described the absorption and emission of radiation for the purposes of atomic spectroscopy and endures in textbooks to this day. From time to time people have re-examined the problem in connection with various experiments and made some small advances toward finding more exact solutions. They have generally found that more exact solutions are not needed, unless exceptionally intense radiation is used. However, more and more intense sources of radiofrequency and microwave radiation have been developed over the years and the recent advent of the laser has made intense, monochromatic sources of radiation at infrared and optical frequencies available. A further study of the interactions of radiation with atomic systems seems appropriate.

The problem to be studied in this thesis is the interaction of a quantum system with a strong oscillating field. By a quantum system we shall mean a system having discrete quantum-mechanical states. The energy spacings of the states are assumed given. Our primary emphasis will be on the probabilities for transitions among these states induced by the field. When no specific example is being discussed, the system will be referred to as an atom, although it could equally well be a single particle with spin, a molecule, or even a more complex aggregate. Only one atom will be treated in interaction with the field. That is, in macroscopic situations involving many atoms the interactions

between atoms will be neglected compared to the interaction with the field. The theory will be best applicable to such physical systems as atomic beams, very low density gases, or dilute impurity atoms in an inert crystal lattice.

By an oscillating field we shall mean a coherent field having well defined frequency and phase. That is, the field amplitude is proportional to $\cos \omega t$. The range of frequencies we can use is limited primarily by the frequency spectra of atoms. The upper limit is the frequency which causes ionization (excites a transition into the continuum). But the lower the frequency, the simpler the theory, since the number of states we need to consider becomes smaller. Our terminology will imply that the field is the electromagnetic field, and in all our applications it will be so. However there is nothing in the formalism which restricts its validity to the electromagnetic field.

The interaction between the atom and the field will be linear in the field amplitude, as in $\vec{p} \cdot \vec{A}$ or $\vec{\mu} \cdot \vec{H}$. The matrix elements of the interaction are assumed known. For brevity they will be indicated by single letters like b , c , and g , which will be proportional to the field amplitude. By a strong oscillating field we shall mean that these interaction matrix elements are appreciable in comparison with the energy separation of the atomic states or with the field frequency, so that the usual perturbation approach is inadequate. An equivalent statement is that the oscillating field strength be comparable to the atomic fields responsible for the state separations.

Kinematics will not be considered. The atoms are to be either at rest or in classical motion. The oscillating field is also at rest; that

is, it consists of standing waves inside a resonant cavity, rather than traveling waves. The atom will be regarded as under the influence of the field for definite periods of time, during which the only time variation of the field strength seen by the atom is the sinusoidal one. In applying the theory to experimental situations, care should be taken to determine whether all the preceding suppositions are met, and especially to ascertain the number of states involved in the interaction and the importance of relaxation phenomena.

Treating the oscillating field as a classical harmonic perturbation, our problem is to solve the time-dependent Schrödinger equation for the amplitudes to be in various states of the atom. From these amplitudes transition probabilities and time-dependent expectation values can be obtained.

We shall concentrate our attention on a very simple case in which only two atomic states, α and β , are coupled by the field. Let the amplitudes that the atom is in these states be $a_\alpha(t)$ and $a_\beta(t)$; the energies, E_α and E_β . Let the matrix elements of the field interaction connecting these states be $2c \cos \omega t$ where c is real. The time-dependent Schrödinger equation is ($\hbar = 1$):

$$i \frac{d}{dt} \psi(t) = \mathcal{H}_C(t) \psi(t)$$

where

$$\psi(t) = \begin{pmatrix} a_\alpha(t) \\ a_\beta(t) \end{pmatrix} \quad \text{and} \quad \mathcal{H}_C(t) = \begin{pmatrix} E_\alpha & 2c \cos \omega t \\ 2c \cos \omega t & E_\beta \end{pmatrix} \quad (1)$$

Suppose that at some initial time t_0 the atom is known to be in the state α : $\psi(t_0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$. Our problem is to solve this pair of coupled differential

equations with such an initial condition. The probability that the atom is in state β at time t can be found as $|a_{\beta}(t)|^2$. This is the transition probability which we wish to study as a function of t , c , ω , and

$$\omega_0 = E_{\alpha} - E_{\beta}.$$

A physical example of this simple case is the following. Consider a spin one half particle with magnetic moment μg . Place it in a uniform magnetic field H_0 in the z direction. Now apply an oscillating field $H_1 \cos \omega t$ in the x direction. The Hamiltonian is $-\vec{\mu} \cdot \vec{H} = \frac{1}{2} \mu g \vec{\sigma} \cdot \vec{H}$. The only states are the two Zeeman levels,* for which $E_{\alpha} = \frac{1}{2} \mu g H_0$, $E_{\beta} = -\frac{1}{2} \mu g H_0$. The interaction matrix element is $2c = \frac{1}{2} \mu g H_1$. By a strong oscillating field we mean that H_1 is comparable to, or even greater than H_0 . Not only can this example be realized in the laboratory, but it also has the advantage of being in principle soluble by classical mechanics, considering the particle as a spinning top with a permanent magnetic dipole moment. This example should be kept in mind throughout the following analysis.

The advances in solving such a problem that have been made since 1927 have appeared from diverse sources and under such diverse titles as "Stark Effect in Rapidly Varying Fields," "Geometrical Representation of the Schrödinger Equation for Solving Maser Problems," and "Transitions Involving Several Electromagnetic Quanta." The most advanced work on the solutions of equations 1 known to the author is the work of Autler and Townes (1). Yet they appear to have overlooked an important feature: the possibility of multiple quantum transitions.

*The words "state" and "level" will be used interchangeably.

These were predicted at about the same time by Winter (2). There thus appears to be as much a need for a correlation of the existing work as for an extension. Parts of this thesis will be devoted to presentation of existing results based on a common starting point. The new material presented is largely an improvement in methods and understanding, rather than a prediction of new phenomena. It is therefore more of academic interest, than of immediate use in describing existing or prospective experiments. The line between original and unoriginal work is hazy, but literature references known to the author will be mentioned wherever applicable.

The logical interconnections of the following chapters are not those of a linear chain, so a few words on what to expect may be helpful. In chapter II we shall review briefly the usual method for treating an oscillatory perturbation and indicate why it is not a suitable method for strong fields. In chapter III we shall present the weak field solution for equations 1 and discuss some of the implications of this form of solution. Chapter IV extends the method of chapter III for finding an approximate time-independent Hamiltonian to problems with more than two atomic levels. The introduction of time-independent perturbation theory then converts the resonance problem for systems with many states to the resonance problem for a system with two states. Chapter V is a short and rather independent one showing how the perturbed energies of a time-independent Hamiltonian may be plotted to display information about the corresponding perturbed wave functions, and in particular to reveal resonances implicit in the approximate Hamiltonians used in

chapters III, IV, VII, and IX.

In chapter VI we prepare a fresh attack on the solution of equations 1 by developing a formal theory for the solutions of the time-dependent Schrödinger equation with a periodic Hamiltonian. Chapter VII then takes the results of chapter VI and combines it with the perturbation method of chapter IV to obtain improved approximate solutions of the two state problem, including solutions for multiple quantum transitions. Chapter VIII is an all out attack on the two state problem using results from chapters V, VI, and VII. Through a variety of analytical approximations plus numerical computations the behavior of the transition probabilities in moderate to really strong fields is elucidated. Chapter IX rests on all the preceding chapters by discussing extensions of the theory so far presented to more complex problems. Finally chapter X looks at the whole business anew from the point of view of quantum field theory. An interesting parallel is drawn between the quantized field formalism and the formalism of chapter VI and greater insight is gained into the physical interpretations of the formulas.

Appendix A gives a derivation of the perturbation theory used in chapters IV, VII, and IX. Appendix B discusses the infinite determinant method of calculating characteristic exponents as it might have been used in chapter VIII.

II. TIME-DEPENDENT PERTURBATION THEORY

In almost every textbook of quantum mechanics equations 1 are solved to first order by time-dependent perturbation theory. The results are used in discussing the emission and absorption of light and are quite adequate for that purpose. We shall review this method of solution briefly here and indicate what might be learned by carrying the calculation to higher order.

The usual procedure of time-dependent perturbation theory is to define the amplitudes with the energy part of the phase factored out. Let $a_\alpha(t) = b_\alpha(t)e^{-iE_\alpha t}$ and $a_\beta(t) = b_\beta(t)e^{-iE_\beta t}$. Then the b 's obey the differential equations:*

$$\begin{aligned} \dot{b}_\alpha &= 2c \cos \omega t e^{i\omega_0 t} b_\beta \\ \dot{b}_\beta &= 2c \cos \omega t e^{-i\omega_0 t} b_\alpha \end{aligned}$$

where the dot denotes time differentiation and $\omega_0 = E_\alpha - E_\beta$. These equations are iterated to obtain a solution as a series in powers of c , starting the iteration with the initial conditions. Taking $b_\alpha = 1$ and $b_\beta = 0$ at $t = 0$ for the initial conditions, the well-known first order result is:

$$b_\beta = \frac{c}{\omega_0 - \omega} \left[e^{-i(\omega_0 - \omega)t} - 1 \right] + \frac{c}{\omega_0 + \omega} \left[e^{-i(\omega_0 + \omega)t} - 1 \right]$$

One usually says that near $\omega = \omega_0$ the first term shows a resonance

*Compare Ref. 3, equation 29.5.

and the second is negligible. Squaring the first term gives the usual transition probability:

$$|b_\beta|^2 = |a_\beta|^2 = \frac{4c^2}{(\omega_0 - \omega)^2} \sin^2 \frac{(\omega_0 - \omega)t}{2}$$

When $(\omega_0 - \omega) < 2c$ this solution can be valid only for limited times, for otherwise it violates unitarity ($|a_\alpha|^2 + |a_\beta|^2 = 1$ at all times). Nevertheless everyone proceeds with it, performing an average over ω or ω_0 , and ending up with a constant transition probability per unit time, sometimes called the Golden Rule, which must also be invalid at large times.

If one tries to carry the perturbation theory to second order one finds

$$\begin{aligned} \dot{ib}_\alpha = & \frac{c^2}{\omega_0 - \omega} e^{2i\omega t} - \frac{2\omega_0 c^2}{\omega_0^2 - \omega^2} e^{i(\omega_0 + \omega)t} + \frac{2\omega_0 c^2}{\omega_0^2 - \omega^2} \\ & - \frac{2\omega_0 c^2}{\omega_0^2 - \omega^2} e^{i(\omega_0 - \omega)t} + \frac{c^2}{\omega_0 + \omega} e^{-2i\omega t} \end{aligned}$$

The constant term will become secular (proportional to t) upon integration, as well as being singular at $\omega = \omega_0$, giving b_α an impossibly large imaginary part. This unpleasantness can be avoided by the following artifice. Redefine the b 's by setting $a_\alpha = b_\alpha e^{-iE_\alpha t - \frac{1}{2} i\Delta\omega t}$ and $a_\beta = b_\beta e^{-iE_\beta t - \frac{1}{2} i\Delta\omega t}$, where $\Delta\omega$ is a quantity yet to be determined. The b 's satisfy

$$\begin{aligned} \dot{ib}_\alpha = & -\frac{1}{2} \Delta\omega b_\alpha + 2c \cos \omega t e^{i(\omega_0 + \Delta\omega)t} b_\beta \\ \dot{ib}_\beta = & 2c \cos \omega t e^{-i(\omega_0 + \Delta\omega)t} b_\alpha + \frac{1}{2} \Delta\omega b_\beta \end{aligned}$$

Iterating we find in first order

$$b_{\beta} = \frac{c}{\omega_0 + \Delta\omega - \omega} \left[e^{-i(\omega_0 + \Delta\omega - \omega)t} - 1 \right] + \text{nonresonant term}$$

In second order we have

$$i\dot{b}_{\alpha} = -\frac{1}{2}\Delta\omega + \frac{2\omega_0 c^2}{\omega_0^2 - \omega^2} + \text{oscillating terms}$$

By choosing $\Delta\omega = 4\omega_0 c^2 / (\omega_0^2 - \omega^2)$, no secular terms will appear in second order. Now look at how this value of $\Delta\omega$ affects b_{β} . Let $2q = \omega_0 + \Delta\omega - \omega$. Substitute for $\Delta\omega$ and square:

$$4q^2 = (\omega_0 - \omega)^2 + \frac{8\omega_0 c^2}{\omega_0 + \omega} + \text{order } c^4$$

Expand around $\omega = \omega_0$:

$$4q^2 = (\omega_0 - \omega)^2 + 4c^2 + \frac{\omega_0 - \omega}{2\omega_0} 4c^2 + \text{higher order}$$

$$4q^2 = \left(\omega_0 - \omega + \frac{c^2}{\omega_0} \right)^2 + 4c^2 + \text{higher order}$$

Finally

$$q \approx \left[\frac{1}{4} \left(\omega - \omega_0 - \frac{c^2}{\omega_0} \right)^2 + c^2 \right]^{1/2}$$

This expression for q remains nonzero as ω is varied through resonance. Putting it into our resonant expression for b_{β} gives us the transition probability

$$|b_{\beta}|^2 = \frac{c^2}{q^2} \sin^2 qt$$

which is less than or equal to one for all ω near ω_0 and all times.

No matter how unconvincing this derivation is, the above result is about the best analytic solution of our problem known for ω near resonance. It suggests that the singular appearance of the perturbation solution is due to a series expansion which does not converge near resonance. Time-dependent perturbation theory is therefore not a desirable method of solution.

Nevertheless if one were so rash as to carry it to third order, one would discover among the morass of terms contributing to b_β the following one:

$$- \frac{c^3 [e^{-i(\omega_0 + \Delta\omega - 3\omega)t} - 1]}{2\omega(\omega_0 + \Delta\omega - \omega)(\omega_0 + \Delta\omega - 3\omega)}$$

Just as our first order solution gave a resonance at $\omega_0 + \Delta\omega - \omega = 0$, this term implies a resonance at $\omega_0 + \Delta\omega - 3\omega = 0$ or $\omega = \frac{\omega_0}{3} + \frac{3c^2}{2\omega_0}$, using the previous value of $\Delta\omega$. Such a subharmonic resonance is called a triple quantum transition, since three photons of frequency ω are required to span the energy difference $\omega_0 + \frac{9c^2}{2\omega_0}$. This particular transition has been observed to occur among the magnetic substates of optically aligned sodium vapor by Margerie and Brossel (4).

Better methods for obtaining these results will be developed in the succeeding chapters.

III. WEAK FIELD SOLUTION -- TWO LEVELS

It is instructive to write out the interaction term in equations 1 in terms of exponentials: $2c \cos \omega t = ce^{i\omega t} + ce^{-i\omega t}$. If but one exponential were present (and its complex conjugate on the other side of \mathcal{H}_C to preserve hermiticity), an elimination of one amplitude from the two coupled equations would lead to a second order differential equation with constant coefficients and an exact solution. Yet with both exponentials present, the amplitudes are so intertwined that the equations resist all attempts to uncover an exact solution in terms of known functions. The reason for this frustrating situation can be elucidated by a transformation which we shall call phase factoring.

Suppose that we define new amplitudes by factoring out from the old ones a time-dependent phase:

$$a_\alpha(t) = e^{-i\mu t} \alpha(t) , \quad a_\beta(t) = e^{-i\nu t} \beta(t)$$

Now all results of physical measurements can be obtained from the density matrix

$$\rho = \begin{pmatrix} \alpha^* \alpha & \alpha^* \beta \\ \beta^* \alpha & \beta^* \beta \end{pmatrix}$$

Suppose we write ρ in terms of α and β instead of a_α and a_β . The diagonal elements, which give transition probabilities, are unaffected by the change, while the off-diagonal elements change by a factor $e^{\pm i(\mu-\nu)t}$. For these off-diagonal elements, which are needed in computing certain expectation values, $\mu - \nu$ must be remembered.

Otherwise μ and ν can be anything we like.

The new amplitudes obey the differential equation

$$i \frac{d}{dt} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} E_\alpha - \mu & ce^{i(\mu-\nu-\omega)t} + ce^{i(\mu-\nu+\omega)t} \\ ce^{-i(\mu-\nu-\omega)t} + ce^{-i(\mu-\nu+\omega)t} & E_\beta - \nu \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

The difference $\mu - \nu$ appears only in the off-diagonal elements, while $\mu + \nu$ appears only in the trace of the new Hamiltonian. Since $\mu + \nu$ does not appear in the density matrix, the trace of the Hamiltonian can have no physical significance. It merely represents a zero point for measuring energy. A convenient round number for the trace is zero. So let $\mu + \nu = E_\alpha + E_\beta$.

If we now choose $\mu - \nu = \omega$, one of the two exponential terms becomes a constant. Solving these relations for μ and ν our new Hamiltonian becomes

$$\begin{pmatrix} \frac{1}{2} (\omega_0 - \omega) & c(1 + e^{2i\omega t}) \\ c(1 + e^{-2i\omega t}) & -\frac{1}{2} (\omega_0 - \omega) \end{pmatrix} = \mathcal{H}_0 + \mathcal{H}_1 \quad (2)$$

where

$$\mathcal{H}_0 = \begin{pmatrix} -\Delta & c \\ c & \Delta \end{pmatrix}, \quad \mathcal{H}_1 = \begin{pmatrix} 0 & ce^{2i\omega t} \\ ce^{-2i\omega t} & 0 \end{pmatrix}, \quad \text{and} \quad \Delta = \frac{1}{2} (\omega - \omega_0)$$

If we had started with only one exponential, our Hamiltonian would have had only the time independent part \mathcal{H}_0 . For a constant Hamiltonian an exact solution can of course be obtained by elementary methods. Only with \mathcal{H}_1 present do we really have differential equations with periodic coefficients and all their attendant complexities.

When we have a weak field ($c/\omega \ll 1$) applied near resonance ($\Delta/\omega \ll 1$) the eigenvalues $\pm p$ of \mathcal{H}_0 are much smaller than ω . Hence \mathcal{H}_1 oscillates very rapidly compared to the behavior of the solution neglecting \mathcal{H}_1 . We would expect that the effect of \mathcal{H}_1 on the solution will average out after a few cycles, so that neglecting it will give us an approximate solution to equations 1. Our phase factoring transformation has thus transformed part of our time-dependent perturbation into a time-independent perturbation which we can use as a first approximation in solving the problem, leaving the remaining time-dependent perturbation for higher approximations. With this program then, let us work the problem $i \frac{d}{dt} \psi = \mathcal{H}_0 \psi$ with $\psi = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$. The effects of \mathcal{H}_1 will be considered in chapters VI to VIII.

Since \mathcal{H}_0 is time independent, it commutes with itself at all times and we can use the formal solution

$$\psi(t) = e^{-i \mathcal{H}_0 t} \psi(0)$$

Now $\mathcal{H}_0^2 = p^2 \mathbf{1}$, where $p^2 = c^2 + \Delta^2$; hence

$$e^{-i \mathcal{H}_0 t} = \cos pt \mathbf{1} - \frac{i}{p} \sin pt \mathcal{H}_0$$

With $\psi(0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, we then have

$$\psi(t) = \begin{pmatrix} \cos pt + i \frac{\Delta}{p} \sin pt \\ -i \frac{c}{p} \sin pt \end{pmatrix}$$

The probability that a transition has occurred to state β by the time t is

$$P_{\beta \leftarrow \alpha} = |\beta(t)|^2 = \frac{c^2}{p^2} \sin^2 pt$$

or

$$P_{\beta \leftarrow \alpha} = \frac{4c^2}{4c^2 + (\omega - \omega_0)^2} \sin^2 [(2c)^2 + (\omega - \omega_0)^2]^{1/2} \frac{t}{2} \quad (3)$$

This equation represents the natural or Rabi line shape of atomic beam spectroscopy (5, 6). We shall refer to it simply as the Rabi formula.

As we shall show in chapters IV and VII equation 3 is a very good representation of the probability for any resonance transition induced by an oscillating field when that resonance is well separated from other resonances. For this reason we shall describe equation 3 in detail.

As a function of time the transition probability oscillates with frequency $2p$ between zero and some maximum. At resonance this maximum is one, i. e. if $\omega = \omega_0$ the transition has taken place with certainty at $t = \pi/2c$. As t progresses the field first induces the atom to jump from state α to state β , then to jump from β back to α , then to β again and so on. The atom just keeps emitting a photon, absorbing one, re-emitting it, etc. as long as the field is applied. If the atom has no other states and no other interactions, there is nothing else it can do.

The dependences on applied frequency ω and energy level separation ω_0 are identical and symmetric. The line shape for $ct = \pi/2$ is shown in figure 1. However the pattern depends strongly on the time t , spreading out with smaller amplitude for shorter times and drawing together with higher lateral peaks for larger times. At some times there is a minimum instead of a maximum at the center. The time average line shape is just the Lorentzian: $\frac{2c^2}{4c^2 + (\omega - \omega_0)^2}$. The half width at half maximum is $2c$, proportional to the strength of the oscillating field.

We will often refer to $2c$ as the width associated with the Rabi formula (equation 3).

To understand still better the Rabi formula, the approximations used to obtain it, and the phase factoring transformation, let us look at our physical example of a spin one half particle in a magnetic field H_0 . We have from chapter I: $\omega_0 = \mu g H_0$, $c = \frac{1}{4} \mu g H_1$. If only one exponential were present, we would have the Hamiltonian

$$\begin{aligned} \mathcal{H}_C &= \begin{pmatrix} \frac{1}{2} \mu g H_0 & \frac{1}{4} \mu g H_1 e^{-i\omega t} \\ \frac{1}{4} \mu g H_1 e^{i\omega t} & -\frac{1}{2} \mu g H_0 \end{pmatrix} \\ &= \frac{1}{2} \mu g [\sigma_z H_0 + \frac{1}{2} \sigma_x H_1 \cos \omega t + \frac{1}{2} \sigma_y H_1 \sin \omega t] \end{aligned}$$

Instead of an oscillating field H_1 in the x direction, this interaction is with a field $\frac{1}{2} H_1$ rotating in the x - y plane with angular frequency ω . The oscillating field is just a superposition of two such fields rotating in opposite directions. In neglecting \mathcal{H}_1 in the derivation of the Rabi formula we were in effect neglecting one rotating field component and retaining the other. For this reason the approximation is usually called the rotating field approximation. It suggests that it is the one rotating field component that actually causes the transition. This view is supported by angular momentum considerations. The two Zeeman levels differ by one in their z component of angular momentum. To conserve angular momentum they must interact with a photon carrying angular momentum in the z direction, i.e. a circularly polarized photon or rotating field.

Our phase factoring transformation can be looked upon as a

transformation of the wave function by the matrix operator

$$\begin{pmatrix} e^{i\mu t} & 0 \\ 0 & e^{i\nu t} \end{pmatrix} = e^{\frac{1}{2} i(E_{\alpha} + E_{\beta})t} \begin{pmatrix} e^{\frac{1}{2} i\omega t} & 0 \\ 0 & e^{-\frac{1}{2} i\omega t} \end{pmatrix}$$

The scalar factor is of no consequence. The matrix factor can be written in terms of spin matrices as

$$\cos \frac{1}{2} \omega t + i\sigma_z \sin \frac{1}{2} \omega t = \exp \left(\frac{1}{2} i\sigma_z \omega t \right) = \exp (iS_z \omega t)$$

This is the rotation operator for rotating a spin one half wave function about the z axis by an angle ωt . The phase factoring transformation in this example is thus seen to be a quantum-mechanical transformation to a rotating coordinate system. In a coordinate system rotating with the field, the field will appear constant, hence the constant Hamiltonian \mathcal{H}_0 . An anti-rotating component of the field will appear in the rotating coordinate system as rotating at twice the frequency, e. g. \mathcal{H}_1 .

Historically the Rabi formula was discovered in just the inverse order to that given here. The problem of magnetic resonance was first treated quantum-mechanically for a rotating field (7, 8, 9). The possibility of extending the Rabi solution to magnetic resonance between states of coupled spins or to electric resonance transitions was not immediately apparent because an exponential type of interaction no longer has a clear physical interpretation in terms of a rotating field. However a derivation of the Rabi formula for a general two-state system was eventually worked out by Torrey (10) as a purely mathematical problem. Current derivations of the Rabi formula (5) just assume an exponential form of interaction and solve the Schrödinger equation. Our

phase factoring method, which is just the mathematical abstraction of the transformation to a rotating coordinate system, helps to show why using only an exponential interaction is a good approximation for the general quantum-mechanical problem.

The magnetic resonance problem can also be solved as a problem in classical gyroscopic motion. By an appropriate association of the classical coordinates with the quantum-mechanical probabilities, it has been found that the correct quantum-mechanical transition probability can be obtained from the classical solution (11). Relatively recently it was shown by Feynman et al. (12) that the general two-state problem is mathematically equivalent to the classical magnetic resonance problem, and hence subject to the same physical visualization.

We shall now discuss in what kinds of physical experiments the Rabi formula plays a role, and why it does not appear in all cases where electromagnetic spectra are studied.

The most direct application of the Rabi formula, and the one for which it was originally derived, is atomic beam resonance spectroscopy. Here one passes a beam of atoms through a state selector which defines their initial state. The beam then traverses a region where the oscillating field is applied, each atom traversing it in a definite time. The beam passes through a second state selector, which determines the final state of the atoms, and finally goes to a detector. During this time atoms within the beam are unlikely to interact or collide with each other. In such an experiment the Rabi formula has been verified in detail (6). Usually the atoms in the beam have a distribution of velocities and spend varying

amounts of time in the oscillating field region. The observed spectral line is then a weighted time average of the Rabi formula (see references 5 and 6 for details). The amplitude of the oscillating field is chosen such that for most atoms $ct \approx \pi/2$ (optimum excitation) and a maximum transition probability is observed. Since the line width is proportional to c , c is a measure of the uncertainty in energy associated with the measurement of the energy level separation ω_0 , while t is the length of time occupied by the measurement. Thus ct equal to the order of one is a manifestation of one of Heisenberg's uncertainty relations.

The advantage of an atomic beam device for spectroscopy is the relative freedom from mutual interactions between different atoms in the beam. Such interactions can broaden or distort the lines relative to those of the free atom. In most other types of spectroscopy interatomic interactions are the principal cause of line width. As a representative, but mathematically simple example we shall consider the effects of collisions in a gas upon the Rabi formula.

Suppose that in a gas in thermal equilibrium the atoms have no interaction except during the short times of actual collisions. Immediately after a collision let the probabilities that the atoms are in either of the two states of interest be determined by the Boltzmann distribution, regardless of the states occupied before the collision. Then the radiation field acts on the atoms to produce transitions only between collisions. If the mean collision time is τ , the probability that an atom will travel for a time t between collisions is $e^{-t/\tau}$ in a Boltzmann gas. The transition probability averaged over this length of interaction time is

$$\begin{aligned}
 R &= \int_0^{\infty} \frac{c^2}{p^2} \sin^2 pt \frac{e^{-t/\tau}}{\tau} dt = \frac{1}{2} \frac{4c^2}{4p^2 + \frac{1}{\tau^2}} \\
 &= \frac{1}{2} \frac{4c^2}{(\omega - \omega_o)^2 + 4c^2 + \frac{1}{\tau^2}} \quad (4)
 \end{aligned}$$

For long times between collisions ($\frac{1}{\tau} \ll c$) we have just the unweighted time average of the Rabi solution. For short times between collisions ($\frac{1}{\tau} \gg c$) the probability reduces to $2c^2 / [(\omega - \omega_o)^2 + \frac{1}{\tau^2}]$. This is the classical Lorentz expression for pressure broadening (13). Since the c^2 in the denominator has been neglected this result could equally well have been obtained from the perturbation theory solution as is usually done. Any other mechanism which effectively makes the time τ the atom is free of transition producing influences other than the oscillating field, small compared to $1/c$ will produce similar results. In emission and absorption spectroscopy there is usually such a relaxation mechanism present.

It is only when our oscillating field is a stronger transition producing influence than relaxation mechanisms that the Rabi formula manifests itself. One effect is the field strength dependent line broadening, sometimes called saturation broadening (14, 15), shown by the $4c^2$ in the denominator of equation 4. Another principal effect is a change in the equilibrium population of the levels. If the thermal probability for being in state α is $\frac{1}{2}(1 - \epsilon)$, its probability in the presence of an exciting field is

$$\bar{P}_{\alpha\alpha} = \frac{1}{2}(1 - \epsilon)(1 - R) + \frac{1}{2}(1 + \epsilon)R = \frac{1}{2}(1 - \epsilon) + \epsilon R \quad (5)$$

where R is given in equation 4. At resonance and in the strong field limit ($c \gg 1/\tau$) R approaches one half and the equilibrium populations of the two levels become equal. The tendency of the radiation field is thus to equalize the populations of the levels, while the collisions tend to restore a Boltzmann distribution. Equation 5 expresses the results of these competing forces. Pumping a system with radiation so strongly as to equalize the state populations is called saturating the transition and finds useful application in maser devices (16). A good discussion of saturation in state populations and also in power absorption has been given by Javan (17, Sec. III).

We noted in our discussion of time-dependent perturbation theory that a constant transition probability per unit time (the Golden Rule) is commonly obtained from the perturbation theory transition probability by performing an average over ω or ω_0 . The perturbation theory transition probability is valid only for limited times, and so is the Golden Rule. But the Rabi formula is valid for all times. By using it in place of the perturbation solution we ought to be able to discover how the Golden Rule is modified at large times to avoid violating unitarity.

Following the argument in Schiff (3, p. 199), we assume that in place of the single state β there are a large number of states β with a density per unit frequency interval $\rho(\omega_0)$ which is nearly constant over a range of a few c about ω . We assume also that the matrix elements between α and each of these states are essentially the same. The total transition probability is

$$\int |a_{\beta}(t)|^2 \rho(\omega_0) d\omega_0$$

with $|a_{\beta}(t)|^2$ given by equation 3. The foregoing assumptions enable us to factor $c^2 \rho$ out of the integral and extend the limits to plus and minus infinity, since the transition probability is strongly peaked at ω . Differentiating we obtain the transition probability per unit time

$$W = \frac{\partial}{\partial t} \left[c^2 \rho(\omega) \int_{-\infty}^{\infty} \frac{\sin^2 pt}{p^2} d\omega_o \right] = 2c^2 \rho(\omega) \int_{\omega}^{\infty} \frac{\sin 2pt}{p} d\omega_o$$

Changing the variable of integration to $y = p/c$ the integral can be evaluated by a formula given in Magnus and Oberhettinger (18). The final result is

$$W = 2\pi c^2 \rho(\omega) J_0^2(2ct)$$

For small times the Bessel function is approximately one and we have just the Golden Rule. For large times the transition probability decreases and oscillates, gradually dying to zero as absorption and stimulated emission occur with nearly equal probability. When relaxation phenomena are present we would have to compute something like

$$\int_0^{\infty} \frac{e^{-t/\tau}}{\tau} 2\pi c^2 \rho(\omega) J_0^2(2ct) dt = \frac{2\pi c^2 \rho(\omega)}{(1+4c^2 \tau^2)^{1/2}}$$

In the usual case of short relaxation time ($c\tau \ll 1$) we have again just the Golden Rule. For strong exciting fields the transition probability is still constant in time, but proportional to c , instead of c^2 . The total integrated transition probability $\int_0^{\infty} W(t) dt$ is $\pi c \rho$, which is the number of states in the frequency interval πc .

IV. WEAK FIELD SOLUTION -- MANY LEVELS

The problem of the interaction of a general system of coupled spins with a rotating magnetic field has been elegantly treated by Salwen (19), using rotating coordinates to obtain a Hamiltonian constant in time. We shall now show how a time independent Hamiltonian describing resonance transitions may be found for any many level situation. The method is to apply a phase factoring transformation to the wave function and then neglect the oscillating part of the new Hamiltonian, exactly as we did in deriving the Rabi Formula.

Suppose we have a Hamiltonian

$$\mathcal{H}_C = \begin{pmatrix} E_\alpha & 2c \cos \omega t & 2d \cos \omega t & \dots \\ 2c \cos \omega t & E_\beta & 2b \cos \omega t & \dots \\ 2d \cos \omega t & 2b \cos \omega t & E_\gamma & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$$

corresponding to the amplitudes $a_\alpha(t)$, $a_\beta(t)$, $a_\gamma(t)$, \dots . We know from first order time-dependent perturbation theory that resonances occur whenever ω is approximately equal to the difference between two energy levels directly connected by the perturbation. From nth order time-dependent perturbation theory resonances occur whenever $n\omega$ is approximately equal to the difference between two energy levels indirectly connected by the perturbation through $n-1$ intermediate states (20). We wish to transform our Hamiltonian so that levels excited at resonance become nearly degenerate and are connected by time-independent matrix

elements. They can then be treated exactly or by time-independent perturbation theory, leaving only non-resonant terms for time-dependent perturbations.

Let us define new amplitudes:

$$\alpha(t) = e^{i\mu t} a_{\alpha}(t)$$

$$\beta(t) = e^{i\nu t} a_{\beta}(t)$$

$$\gamma(t) = e^{i\xi t} a_{\gamma}(t)$$

As noted in the two level problem these new amplitudes are just as good as the old ones for computing transition probabilities. The new amplitudes obey a Schrödinger equation with the Hamiltonian \mathcal{H}' :

$$\mathcal{H}' = \begin{pmatrix} E_{\alpha} - \mu & 2c \cos \omega t e^{i(\mu-\nu)t} & 2d \cos \omega t e^{i(\mu-\xi)t} & \dots \\ 2c \cos \omega t e^{-i(\mu-\nu)t} & E_{\beta} - \nu & 2b \cos \omega t e^{i(\nu-\xi)t} & \dots \\ 2d \cos \omega t e^{-i(\mu-\xi)t} & 2b \cos \omega t e^{-i(\nu-\xi)t} & E_{\gamma} - \xi & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$$

By choosing $\mu + \nu + \xi + \dots = E_{\alpha} + E_{\beta} + E_{\gamma} + \dots$ we can make the trace of \mathcal{H}' anything we like. By choosing $\mu - \nu = \omega$ we can transform $2c \cos \omega t$ into $c(1 + e^{2i\omega t})$. At the same time $(E_{\alpha} - \mu) - (E_{\beta} - \nu)$ becomes $E_{\alpha} - E_{\beta} - \omega$. If α and β are near resonance with frequency ω , this difference is small compared to ω . Thus setting $\mu - \nu = \omega$ accomplishes both objectives outlined above. We can do the same for each pair of levels in resonance and perhaps others.

Note that $\mu - \nu = \omega$, $\nu - \xi = \omega$, $\mu - \xi = \omega$ would be inconsistent equations. Not all oscillating off diagonal elements can be converted

from $2 \cos \omega t$ to $(1 + e^{\pm 2i\omega t})$. But levels α and γ cannot be resonant with frequencies ω and 2ω both. So we use $\mu - \xi = \omega$ or 2ω , depending on which is nearest resonance, and let other matrix elements remain entirely oscillatory. Thus different phase factorings may be desirable for different ranges of ω . In most practical cases, however, selection rules will make enough off diagonal elements zero so that one phase factoring will cover all resonances of interest.

Having suitably evaluated the phase constants μ, ν, \dots we write \mathcal{H}' as $\mathcal{H}_0 + \mathcal{H}_1$, where \mathcal{H}_0 is constant and includes the resonances of interest. \mathcal{H}_1 is purely oscillatory and will be neglected for the present. The effects of including \mathcal{H}_1 will be considered in chapter IX and found to be small if b, c, d, \dots are much less than ω .

The problem has now been reduced to one with a constant Hamiltonian. To solve the Schrödinger equation we need to find $\exp(-i \mathcal{H}_0 t)$, which can be done by diagonalizing \mathcal{H}_0 . Due to the algebraic awkwardness of expressing the roots of cubic and higher degree polynomials, we shall not attempt to analytically diagonalize anything bigger than a two by two matrix. Instead we shall use the perturbation theory in Appendix A to reduce larger matrices to two by two. This will enable us to treat all resonances which are well separated from each other. When resonance lines overlap, the reduction to only two states is no longer a good approximation.

To avoid repetition we shall compute the exponential function of a two by two matrix once and for all. If we are studying an n -quantum transition between two states, say α and β , we obtain after phase factoring and perturbation reduction to two by two size a hermitian matrix

of the form

$$\mathcal{H}_2 = \begin{pmatrix} E_a + \delta_a & \frac{1}{2} u \\ \frac{1}{2} u^* & E_\beta + \delta_\beta + n\omega \end{pmatrix} + \text{multiple of unit matrix} \quad (6)$$

where δ_a and δ_β are level shifts due to interactions with other states and $\frac{1}{2} u$ is the n th order matrix element connecting the two states.

We can write this in terms of the Pauli σ matrices, letting d be the difference of the diagonal elements

$$\mathcal{H}_2 = E_0 \mathbf{1} + \frac{1}{2} d \sigma_z + \frac{1}{2} \text{Re}(u) \sigma_x - \frac{1}{2} \text{Im}(u) \sigma_y$$

The unit matrix commutes with all the others and can thus be algebraically separated out:

$$\exp(-i \mathcal{H}_2 t) = \exp(-i E_0 t) \exp\left[-i(d\sigma_z + \text{Re}(u)\sigma_x - \text{Im}(u)\sigma_y)\frac{t}{2}\right]$$

The σ matrices anticommute, hence

$$(d\sigma_z + \text{Re}(u)\sigma_x - \text{Im}(u)\sigma_y)^2 = d^2 + \text{Re}(u)^2 + \text{Im}(u)^2 \equiv r^2$$

We use this relation to simplify powers of the σ matrices in the series expansion of the exponential, obtaining finally

$$\begin{aligned} \exp(-i \mathcal{H}_2 t) = \exp(-i E_0 t) & \left[\cos \frac{rt}{2} \right. \\ & \left. - i \frac{(d\sigma_z + \text{Re}(u)\sigma_x - \text{Im}(u)\sigma_y)}{r} \sin \frac{rt}{2} \right] \end{aligned}$$

If the initial state is α , the wave function at time t is

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \exp(-i H_2 t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = e^{-i E_0 t} \begin{pmatrix} \cos \frac{rt}{2} & -i \frac{d}{r} \sin \frac{rt}{2} \\ i \frac{u}{r} \sin \frac{rt}{2} & \cos \frac{rt}{2} \end{pmatrix}$$

The transition probability is $|\beta|^2 = \frac{|u|^2}{r^2} \sin^2 \frac{rt}{2}$. If we write ω_{res} for $E_\alpha + \delta_\alpha - E_\beta - \delta_\beta$, we can express the result as

$$P_{\beta \leftarrow \alpha} = \frac{|u|^2}{(\hbar\omega - \omega_{\text{res}})^2 + |u|^2} \sin^2 [(\hbar\omega - \omega_{\text{res}})^2 + |u|^2]^{1/2} \frac{t}{2} \quad (7)$$

Equation 7 is the generalization of the Rabi formula to multiple quantum transitions. It has been given previously by Hack (20), Salwen (19), and by Winter (21), but always for a limited class of resonance transitions. The present formulation reveals it to be valid for any transition where resonance exists between only two levels. In discussing specific examples henceforth we shall not write out equation 7, but merely write down the resonance frequency ω_{res} and line width parameter u to be substituted therein by comparing the two by two matrix approximating our problem with Eq. 6.

As an explicit example consider a three level problem:

$$H_C = \begin{pmatrix} E_\alpha & 2c \cos \omega t & 0 \\ 2c \cos \omega t & E_\beta & 2b \cos \omega t \\ 0 & 2b \cos \omega t & E_\gamma \end{pmatrix}$$

These levels might, for instance, be the Zeeman sublevels of the $F = 1$ hyperfine state in the electronic ground state of atomic hydrogen. The central level β could be shifted from the midpoint between levels α and

γ by the quadratic Zeeman effect, yet $E_\alpha - E_\beta$ could still be small compared to the separation between the $F = 1$ triplet states, and the $F = 0$ singlet state which we would be neglecting.

We perform the phase factoring transformation with

$\mu = (E_\alpha + E_\beta + E_\gamma + 3\omega)/3$, $\nu = (E_\alpha + E_\beta + E_\gamma)/3$, $\xi = (E_\alpha + E_\beta + E_\gamma - 3\omega)/3$ obtaining

$$\mathcal{H}'_C = \begin{pmatrix} \Delta - \frac{a}{3} & c & 0 \\ c & \frac{2a}{3} & b \\ 0 & b & -\Delta - \frac{a}{3} \end{pmatrix} + \begin{pmatrix} 0 & ce^{2i\omega t} & 0 \\ ce^{-2i\omega t} & 0 & be^{2i\omega t} \\ 0 & be^{-2i\omega t} & 0 \end{pmatrix} \quad (8)$$

where $\Delta = \frac{1}{2}(E_\alpha - E_\gamma) - \omega$ and $a = \frac{1}{2}(2E_\beta - E_\alpha - E_\gamma)$. The energy level scheme and meanings of the parameters a and Δ are illustrated in figure 2. We neglect the oscillating part of \mathcal{H}'_C until chapter IX and consider two cases.*

Consider first the case where we have a resonance between levels α and β . Then $\Delta \approx a$ and the first two levels in \mathcal{H}'_C are nearly degenerate, while the third is $2a$ away. If $a \gg b, c$ we can treat the third level by the perturbation theory of Appendix A, reducing the problem to a two level one (equation A8):

$$\begin{pmatrix} \Delta - \frac{a}{3} & c \\ c & \frac{2a}{3} + \frac{b^2}{2a} \end{pmatrix}$$

The transition probability $P_{\beta \leftarrow \alpha}$ is then given by equation 7 with $n = 1$,

*This particular three level problem has been studied in more detail by Besset *et al.* (22), but they do not clearly indicate how they arrive at their results.

$$\omega_{\text{res}} = E_{\alpha} - E_{\beta} - b^2 / [(E_{\beta} - E_{\gamma}) - (E_{\alpha} - E_{\beta})] \quad (\text{or } \Delta = a + \frac{b^2}{2a}), \text{ and } u = 2c.$$

The effect of the interaction with the third level γ has been to shift the energy of the level β and thus the resonance frequency. When the above approximate solution is valid, the α, β resonance is well separated from the β, γ resonance and the level shift is only a small fraction of the line width. As a decreases the shift increases, but never becomes larger than the line width $2c$.

Consider next the case where we have a double quantum transition between states α and γ . For this case we have $\Delta \ll a$ and the first and third levels in \mathcal{H}'_C are nearly degenerate. If again $a \gg b, c$ we can treat the second level by perturbation theory obtaining the two level matrix

$$\begin{pmatrix} \Delta - \frac{a}{3} - \frac{c^2}{a} & -\frac{bc}{a} \\ -\frac{bc}{a} & -\Delta - \frac{a}{3} - \frac{b^2}{a} \end{pmatrix}$$

The transition probability from state α to γ is again given by equation 7 with $n = 2$, $u = \frac{2bc}{a}$, and $\omega_{\text{res}} = E_{\alpha} - E_{\gamma} + 2(b^2 - c^2) / [(E_{\beta} - E_{\gamma}) - (E_{\alpha} - E_{\beta})]$ (or $\Delta = (c^2 - b^2) / 2a$). The width is much smaller than that for the single quantum transition and hence requires greater excitation powers (larger b, c) to observe. But with $ut \approx \pi$ the transition probability $P_{\gamma \leftarrow \alpha}$ can be close to one while $P_{\beta \leftarrow \alpha}$ is still quite small. As a decreases the width of the double quantum resonance increases. Also the single quantum resonance to state β approaches the double quantum resonance. When the two lines overlap it becomes possible for the system to reach state γ by two successive real single quantum transitions with appreciable

populating of state β . This process then competes with the double quantum transition, which goes virtually through state β without appreciably populating it, making a more complicated line shape. However for large a the single and double quantum resonances are quite distinct.

When $a = 0$ there is no longer any distinction between two successive single quantum transitions and one double quantum transition. This special case arises in the Zeeman effect of particles with spin one. However Majorana has shown that the transition probabilities between any two magnetic substates of a particle of arbitrary spin can be expressed in terms of the transition probability in the spin one half case (23, 24). So for simple Zeeman spectra we need solve only a two state problem. Unfortunately Majorana's result does not extend to coupled spins.

To give a better feeling for the magnitudes involved we have evaluated an example from radio frequency spectroscopy in terms of experimental quantities. Suppose we are observing magnetic resonance between the three Zeeman sublevels of the $F = 1$ hyperfine state of atomic hydrogen, using an atomic beam spectrometer. In a static field H_0 of 8 gauss the levels are spaced by about 11 megacycles with the $m_F = 0$ level shifted 86 kilocycles from the midpoint between the $m_F = \pm 1$ levels by the quadratic Zeeman effect. The $\Delta m_F = \pm 1$ transitions are excited by an oscillating field $H_1 \cos \omega t$ perpendicular to H_0 . Suppose that the transit time of the atoms through the apparatus is such that $H_1 = 8.5$ milligauss gives a maximum transition probability with a line width of about 15 kc. In such a situation the ratio c/a is 0.05 so our approximate solution should describe the experiment adequately. The ratio c/ω is 4×10^{-4} , so the neglect of the anti-rotating component of the

exciting field is a very good approximation.

The two primary resonances $1 \longleftrightarrow 0$ and $0 \longleftrightarrow -1$ will appear as distinct peaks about 170 kc apart, both with 15 kc line widths since the matrix elements b and c are nearly equal. The frequency shifts of the peaks due to the presence of a third level amount to only 100 cps. The double quantum transition $1 \longleftrightarrow -1$ will fall midway between the two primary resonances and would be barely discernible at only one twentieth the height of the other peaks.

Upon increasing the rf power by a factor twenty (increasing H_1 to 40 milligauss) the double quantum transition will be excited optimally. It will then have about the same peak amplitude as the other resonances, and a width of about $7\frac{1}{2}$ kc (one half of 15 kc because $n = 2$ in equation 5). The primary resonances will each have broadened to about 70 kc widths and been shifted away from each other by about 2 kc.

Although double quantum transitions were studied theoretically by Goeppert-Mayer (25) more than thirty years ago, they were not observed in the laboratory until 1950 (26). An experiment similar to the one just envisaged, but with a slightly more complicated spectrum, has been performed by Kusch on the hyperfine levels of K^{39} and several double quantum transitions were observed (27). Salwen's analysis (19) was directed toward the explanation of Kusch's results. The most complete discussions of multiple quantum transitions available are in the article by Hack (20) and in the Handbuch der Physik article on atomic and molecular beams (6). Double quantum transitions have recently been observed in the optical region with the aid of laser light sources (28, 29).

V. INTERPRETATION OF EIGENVALUE PLOTS

In their work on the problem of resonances in a many level system, Besset, Horowitz, Messiah and Winter (22) described a most remarkable behavior of the eigenvalues and eigenfunctions of the Hamiltonian as ω passed through a resonance. For example in figure 3 we show a plot of the eigenvalues (curves) and diagonal elements (straight lines) of the two-state Hamiltonian \mathcal{H}_0 used in obtaining equation 3. The eigenvalues form a hyperbola, with resonance in the transition occurring at the position of closest approach of the two branches. The distance of closest approach is $2c$ or the width of the resonance. Asymptotically the eigenvalues approach the values they would have if there were no interaction (straight lines in the figure), except they have switched identities in going from one side of the resonance to the other. The accompanying eigenvectors reflect this change in identity. In figure 4 we show the eigenvalues and diagonal elements of the three level Hamiltonian discussed in the preceding chapter. The eigenvalues are nearly the same as the diagonal elements except when they come close to each other, as they do near $\Delta = a, 0, -a$. It was at these places that we found resonances. The following analysis, which has not been given by other authors, will show how much may be learned about eigenvectors and transitions from perusal of such a graph of the eigenvalues.

Consider a hermitian matrix \mathcal{H} , such as might be obtained from a phase factoring transformation as described in the preceding chapter. Write its diagonal elements E_m as $a_m y + b_m$, where the a_m

are simple numbers (e.g. $\pm \frac{1}{2}$). Then $\partial \mathcal{H}/\partial y$ is a diagonal matrix with elements a_m . The off diagonal elements of \mathcal{H} will be regarded as a perturbation. We introduce Dirac notation for the normalized eigenvectors. Thus $|m\rangle$ is the eigenvector of the unperturbed (diagonal) matrix corresponding to the eigenvalue E_m , and $|\lambda_m\rangle$ is the eigenvector of the full matrix corresponding to the eigenvalue λ_m . In this notation the eigenvalue equation is

$$\mathcal{H}|\lambda_m\rangle = \lambda_m |\lambda_m\rangle \quad (9)$$

If we plot E_m as a function of y we find a straight line of slope a_m . In a simultaneous plot of all E_m each line can be associated with a state $|m\rangle$ by its slope a_m . For a small perturbation the eigenvalues λ_m plotted as functions of y should lie close to the E_m and therefore be subject to the same identification rules.

To show this analytically we differentiate equation 9 with respect to y :

$$\frac{\partial \mathcal{H}}{\partial y} |\lambda_m\rangle + \mathcal{H} \frac{\partial}{\partial y} |\lambda_m\rangle = \frac{\partial \lambda_m}{\partial y} |\lambda_m\rangle + \lambda_m \frac{\partial}{\partial y} |\lambda_m\rangle$$

The eigenvectors form a complete basis, hence we can expand their derivatives:

$$\frac{\partial}{\partial y} |\lambda_m\rangle = \sum_k C_{mk} |\lambda_k\rangle \quad (10)$$

\mathcal{H} can now operate on $|\lambda_k\rangle$, giving us after transposition

$$\frac{\partial \mathcal{H}}{\partial y} |\lambda_m\rangle = \frac{\partial \lambda_m}{\partial y} |\lambda_m\rangle + \sum_k C_{mk} (\lambda_m - \lambda_k) |\lambda_k\rangle$$

Taking the inner product with $\langle \lambda_m|$ and $\langle \lambda_k|$ respectively we obtain

$$\frac{\partial \lambda_m}{\partial y} = \langle \lambda_m | \frac{\partial \mathcal{H}}{\partial y} | \lambda_m \rangle \quad (11)$$

and

$$C_{mk} = \frac{\langle \lambda_k | \frac{\partial \mathcal{H}}{\partial y} | \lambda_m \rangle}{\lambda_m - \lambda_k} \quad (k \neq m) \quad (12)$$

Since $\partial \mathcal{H} / \partial y$ is diagonal in the unperturbed representation we can evaluate equation 11 in the form

$$\frac{\partial \lambda_m}{\partial y} = \sum_i a_i |\langle i | \lambda_m \rangle|^2 \quad (13)$$

Since $\sum_i |\langle i | \lambda_m \rangle|^2 = 1$ from the normalization, $\partial \lambda_m / \partial y$ must lie between the maximum and minimum values of a_i . If in a certain range of y values $|\lambda_m\rangle$ is predominantly state $|n\rangle$ with admixtures of other states of order ϵ , then equation 13 becomes $\partial \lambda_m / \partial y = a_n + O\epsilon^2$.

Thus the slope of $\lambda_m(y)$ gives information about the components of its eigenvector.

By differentiating equation 9 twice and using equations 10 and 12 we obtain

$$\frac{\partial^2 \lambda_m}{\partial y^2} = 2 \sum_{k \neq m} \frac{|\langle \lambda_m | \frac{\partial \mathcal{H}}{\partial y} | \lambda_k \rangle|^2}{\lambda_m - \lambda_k} \quad (14)$$

If $|\lambda_m\rangle$ is predominantly state $|n\rangle$, $\partial^2 \lambda_m / \partial y^2$ is of order ϵ^2 . Thus a nearly pure state is identified by a nearly constant slope of some a_i . In figures 3 and 4 we find examples of this where the curves are well separated. The states are labeled along the asymptotes.

As λ_m and λ_k approach each other, their second derivatives

become large, bending the curves away from each other. Barring accidental degeneracy the curves do not cross as the unperturbed E_m do. The principal exception occurs when the states $|m\rangle$ and $|k\rangle$ are in no way coupled by the perturbation, in which case $\langle \lambda_m | \frac{\partial \mathcal{H}}{\partial y} | \lambda_k \rangle$ is identically zero.

If $|\lambda_m\rangle$ and $|\lambda_k\rangle$ are nearly pure unperturbed states as they approach each other from either side, we expect they will mix only with each other when they are close together. We can then analyze their behavior by making a two-state approximation. Introduce $A(y)$ to denote the degree of mixing of the two states. Our two state approximation becomes explicitly

$$\begin{aligned} \langle m | \lambda_m \rangle &= \sqrt{(1-A)/2} - O\epsilon^2 & \langle m | \lambda_k \rangle &= e^{-i\theta} \sqrt{(1+A)/2} - O\epsilon^2 \\ \langle k | \lambda_m \rangle &= e^{i\theta} \sqrt{(1+A)/2} - O\epsilon^2 & \langle k | \lambda_k \rangle &= -\sqrt{(1-A)/2} - O\epsilon^2 \\ \langle i | \lambda_m \rangle &= O\epsilon & i \neq k, m & \quad \langle i | \lambda_k \rangle = O\epsilon \quad i \neq k, m \end{aligned} \quad (15)$$

These forms are largely dictated by orthonormality. As A varies from -1 to +1 $|\lambda_m\rangle$ changes from $|m\rangle$ to $|k\rangle$ and $|\lambda_k\rangle$ from $|k\rangle$ to $|m\rangle$.

The behavior of A and the eigenvalues as a function of y can be recovered entirely from equations 11 and 14 in this two-state approximation. The derivatives are

$$\begin{aligned} \frac{\partial \lambda_m}{\partial y} &= \frac{1-A}{2} a_m + \frac{1+A}{2} a_k + O\epsilon^2 \\ \frac{\partial \lambda_k}{\partial y} &= \frac{1+A}{2} a_m + \frac{1-A}{2} a_k + O\epsilon^2 \end{aligned}$$

$$\frac{\partial^2 \lambda_m}{\partial y^2} = \frac{1 - A^2}{2} \frac{(a_m - a_k)^2}{\lambda_m - \lambda_k} + O\epsilon^2$$

$$\frac{\partial^2 \lambda_k}{\partial y^2} = \frac{1 - A^2}{2} \frac{(a_k - a_m)^2}{\lambda_m - \lambda_k} + O\epsilon^2$$

Let $\lambda_m - \lambda_k = r$. Then $\partial r / \partial y = A(a_k - a_m) + O\epsilon^2$ and

$$\frac{\partial^2 r}{\partial y^2} = \frac{1 - A^2}{r} (a_m - a_k)^2 = \frac{(a_m - a_k)^2 - (\partial r / \partial y)^2}{r}$$

This differential equation can be readily solved, yielding

$$r^2 = (a_m - a_k)^2 (y - y_r)^2 + u^2 + O\epsilon^2 \quad (16)$$

where y_r and u are constants of integration. Evidently y_r is the value of y at minimum separation and u is the value of the separation.

Since $\frac{\partial \lambda_m}{\partial y} + \frac{\partial \lambda_k}{\partial y} = a_m + a_k$ is constant we can integrate to get $\lambda_m + \lambda_k$ and combine with r to find the individual eigenvalues

$$\lambda_m = E_0 + \frac{1}{2} (a_m + a_k) y + \frac{1}{2} r$$

$$\lambda_k = E_0 + \frac{1}{2} (a_m + a_k) y - \frac{1}{2} r$$

Thus in the vicinity of resonance the eigenvalues form a little hyperbola, with corrections dependent only on the squares of amplitudes for admixtures of other states.

As $(y - y_r)$ passes from large (compared to u) negative to large positive values, $A = \frac{1}{2} (a_k - a_m)(y - y_r)/r$ goes from -1 to +1 and the eigenvectors exchange their identity in terms of unperturbed states.

This behavior is characteristic of a resonance.

Knowing A , and from it the amplitudes in equation 15, we can actually solve the resonance problem. Suppose that at time $t = 0$ the system is in state

$$|m\rangle = \sqrt{(1-A)/2} |\lambda_m\rangle + e^{i\theta} \sqrt{(1+A)/2} |\lambda_k\rangle + O\epsilon$$

Then at time t the system is in state

$$|t\rangle = \sqrt{(1-A)/2} e^{-i\lambda_m t} |\lambda_m\rangle + e^{i\theta} \sqrt{(1+A)/2} e^{-i\lambda_k t} |\lambda_k\rangle + O\epsilon$$

The probability of transition to state $|k\rangle$ can be evaluated as

$$P_{k \leftarrow m} = |\langle k|t\rangle|^2 = \frac{u^2}{r^2} \sin^2 \frac{rt}{2} + \text{order } \epsilon^2$$

With a suitable definition of y and y_r this agrees with equation 7.

This should not be surprising since the same approximation, that of two states, was used in both derivations.

Thus if we are looking for resonances in a complicated many level problem we can first plot out the eigenvalues as a function of a y -like parameter. From the graph we can identify states and locate resonances, even when shifts are large. In figure 4 note how the different widths of the resonances and the shift of the central one show up. (Unshifted value is at the intersection of the straight lines.) If three or more levels are comparably close and representing mixed states in some region, we know we have to treat them exactly; yet we may still be able to neglect some states which are far away. Even though the eigenvalues are obtained by an electronic computer and a three or four level Schrödinger equation

must be subsequently solved by the computer, we have gained much by finding where to look for which resonances. A blind computer attack suffers from the fact that the transition probabilities for given parameters depend sensitively on the time.

The results of this chapter will be of particular benefit in ferreting out the strong field behavior of equations 1 in chapter VIII.

VI. THE SCHRÖDINGER EQUATION WITH PERIODIC HAMILTONIAN

The lowest order effects of including \mathcal{H}_1 in the solution of equations 2 were first successfully determined by Bloch and Siegert for the case of magnetic resonance (30). They found oscillating terms of the order $\frac{c}{\omega} e^{2i\omega t}$ appearing in the amplitudes and a change in the transition rate frequency ω . They then noted that in atomic beam devices the atoms enter the radiation field in a continuous stream. The times of entry t_0 , and hence the initial phase of the oscillating field seen by the atoms, are different. What one should compute is a transition probability averaged over the initial phase of the field, or equivalently over the initial times t_0 , keeping the elapsed time $t - t_0$ fixed. This average is distinct from one over the elapsed times required if the atoms have a distribution of velocities. On averaging their probability over t_0 Bloch and Siegert found that the oscillating terms go out in first order, leaving a transition probability of just the Rabi form (equation 3) except that ω_0 is replaced by $\omega_0 + \frac{c^2}{\omega_0}$. This so-called Bloch-Siegert shift in the peak of the resonance is a small fraction of the line width, and becomes a smaller fraction as c/ω_0 is reduced to increase the accuracy of the measurement of ω_0 . Hence it is of no importance in precision spectroscopy (31).

Bloch and Siegert's result has been rederived by a variety of methods (32, 33, 1, 31, chapter II of this thesis), all shorter than the original one. But after much study we have developed a method so much superior that a third order solution can be obtained with less effort than Bloch and Siegert expended on their first order solution. In order to

understand this method we must first develop a formal theory for the time-dependent Schrödinger equation with a periodic Hamiltonian. Then in chapter VII we shall rederive the Bloch-Siegert solution with unprecedented ease.

We shall study the general properties of the time-dependent Schrödinger equation with a periodic Hamiltonian in matrix form. That is, we seek solutions of

$$i \frac{d}{dt} \psi(t) = \mathcal{H}_C(t) \psi(t) \quad (17)$$

where \mathcal{H}_C is an N by N hermitian matrix of periodic functions of t with period T or frequency ω ($\omega T = 2\pi$), and ψ is an N by 1 column matrix of the probability amplitudes. The components of \mathcal{H}_C and ψ will be denoted by Greek letters $\alpha, \beta, \gamma, \dots$ corresponding to the atomic states. The matrix equation 17 is just a shorthand way of writing N simultaneous first order differential equations. Such a system has N linearly independent solutions. These N solutions can be used to form the columns of a square matrix $X(t)$ which satisfies the Schrödinger equation and is non-singular.

Since the Schrödinger equation is linear, any linear combination of the N solutions in $X(t)$ is also a solution. In matrix notation a linear combination is achieved by multiplying $X(t)$ on the right by a matrix of constants. Of particular interest is the matrix $U(t; t_0) = X(t)X^{-1}(t_0)$ which obeys the Schrödinger equation and the initial conditions $U(t_0; t_0) = 1$. For the solution of equation 17 is

$$\psi(t) = U(t; t_0) \psi(t_0)$$

that is, $U(t; t_0)$ describes the evolution in time of an arbitrary state $\psi(t_0)$. The components of U can be directly interpreted in terms of probability amplitudes. For instance $U_{\beta\alpha}(t; t_0)$ is the probability amplitude that a system initially in state α at time t_0 , will be in state β at time t .

Since \mathcal{H}_C is a hermitian operator, the normalization $\psi^\dagger(t)\psi(t)$, or more generally $X^\dagger(t)X(t)$, is constant in time. In the case of $U(t; t_0)$ this constant is the unit matrix, since we can evaluate it at $t = t_0$. Therefore $U(t; t_0)$ is a unitary matrix for all t . By multiplying on the right by a constant unitary matrix, many other unitary solutions of equation 17 can be obtained.

Since \mathcal{H}_C is a periodic function of the independent variable, we can apply the Floquet theory for differential equations with periodic coefficients. Two other authors (32, 1) have used Floquet's theorem in connection with the present problem, but neither carried it to the extremes about to be described. We shall first derive Floquet's theorem in matrix notation.*

Let $X(t)$ be a solution of equation 18

$$i \frac{d}{dt} X(t) = \mathcal{H}_C(t)X(t) \quad (18)$$

Replace t by $t + T$. Since \mathcal{H}_C is unchanged, $X(t + T)$ is a solution of the same equation as $X(t)$. Hence they must be related by a constant matrix: $X(t + T) = X(t)A$. Let A be diagonalized by the unitary matrix R .** Write its eigenvalues as exponentials $e^{-iq_\alpha T}$. Then

* Since this derivation was first worked out, a matrix representation of Floquet's theorem has appeared in the literature (34). A rigorous treatment in terms of coupled first order equations is given by Moulton (35).

** If this is not possible, see Moulton (35).

$$R^{-1}AR = e^{-iQT}$$

where Q is a diagonal matrix with elements q_a . We now have

$$X(t + T) = X(t) R e^{-iQT} R^{-1}$$

Multiply on the right by $R e^{iQ(t + T)}$

$$X(t + T) R e^{iQ(t + T)} = X(t) R e^{iQt}$$

If the right hand side is denoted by $\Phi(t)$, then the left hand side is $\Phi(t + T)$, or Φ is a periodic function of time. Thus there exists a solution of equation 18, namely $X(t)R$, of the form $\Phi(t)e^{-iQt}$ where $\Phi(t)$ is periodic and Q is diagonal. This is Floquet's theorem in matrix form. The components of the solution $\Phi_{\alpha\beta}(t)e^{-iq_{\beta}t}$ are in the form given in the usual treatment of Floquet's theorem. The q 's are called characteristic exponents. Their determination is the major obstacle to the solution of differential equations with periodic coefficients.

In our problem \mathcal{H}_C is both periodic and hermitian. Hence we could have used the unitary matrix $U(t; t_0)$ in the above proof. Then A becomes a unitary matrix (namely $U(t_0 + T; t_0)$) and can always be diagonalized by a unitary transformation R . Its diagonal form is also unitary, i.e. the matrix Q must be hermitian, or the characteristic exponents real. This is in contrast with the case of the Mathieu or Hill equations where the characteristic exponent may be either real or complex, depending on the values of certain parameters. With $X(t)$, R , and e^{-iQt} all unitary, $\Phi(t)$ is unitary and we can strengthen Floquet's theorem to say there exists a unitary solution of equation 18:

$F(t) = \Phi(t) e^{-iQt}$. The special solution U can then be written in terms of F :

$$U(t; t_0) = F(t)F^{-1}(t_0) = \Phi(t)e^{-iQ(t-t_0)}\Phi^{-1}(t_0)$$

A relation exists between the determinant of $U(t; t_0)$ and the trace of $\mathcal{H}_C(t)$. The formal solution for U is

$$U(t_1; t_0) = P \exp \left(-i \int_{t_0}^{t_1} \mathcal{H}_C(t) dt \right) \quad (19)$$

where the P indicates the time ordered product of the matrices in the integral. If we write the integral as a limit of a sum, then the exponential of the sum becomes a product of exponentials. The determinant of U is the product of the determinants of the exponentials. The determinant of the exponential of a matrix is the exponential of the trace of the matrix. Making this substitution we can put the product of exponentials back into the form of an exponential of an integral and drop the P , since we now have ordinary commutative numbers instead of matrices. The final result is

$$\det U(t_1; t_0) = \exp \left(-i \int_{t_0}^{t_1} \text{Tr } \mathcal{H}_C(t) dt \right)$$

In particular the determinant of A is

$$\det A = \det U(t_0 + T; t_0) = \exp \left(-i \int_{t_0}^{t_0 + T} \text{Tr } \mathcal{H}_C(t) dt \right)$$

But the determinant of A also equals the product of its eigenvalues

$$\det A = \prod_a \exp(-iq_a T) = \exp \left(-i \sum_a q_a T \right)$$

Equating the two exponential forms for $\det A$ we find that the sum of the characteristic exponents becomes, within an integral number of ω 's, just the time average of the trace of \mathcal{H}_C ,

$$\sum_{\alpha} q_{\alpha} = \frac{1}{T} \int_{t_0}^{t_0+T} \text{Tr } \mathcal{H}_C(t) dt \quad (\text{mod } \omega) \quad (20)$$

As discussed in chapter IV we can make the trace of \mathcal{H}_C anything we like, so that we have one free relation among the characteristic exponents. In the case of two atomic states in chapter III we chose the trace to be zero, because we then have $q_{\beta} = -q_{\alpha}$, hence only one characteristic exponent to determine.

From equation 19 we also see that if \mathcal{H}_C is symmetric at all times, then U is symmetric. In these cases the transition probability $P_{\beta \leftarrow \alpha} = |U_{\beta\alpha}|^2$ is the same as the inverse transition probability $P_{\alpha \leftarrow \beta}$. For a two state system the unitarity of U makes these transition probabilities equal whether \mathcal{H}_C is symmetric or not.

Next we shall show how the problem of determining the unitary Floquet solution $F(t)$ of equation 18 can be reduced to an eigenvalue, eigenvector problem for an infinite matrix. We write F in component form:

$$F_{\alpha\beta}(t) = \Phi_{\alpha\beta}(t) e^{-iq_{\beta}t}$$

We expand the periodic function $\Phi_{\alpha\beta}$ in Fourier series with coefficients $F_{\alpha\beta}^n$:

$$F_{\alpha\beta}(t) = \sum_n F_{\alpha\beta}^n e^{in\omega t} e^{-iq_{\beta}t}$$

We also expand the components of \mathcal{H}_C in Fourier series:

$$(\mathcal{H}_C)_{\alpha\beta} = \sum_n \mathcal{H}_{\alpha\beta}^n e^{in\omega t}$$

Substituting into equation 18 we get an infinite set of recursion relations for the $F_{\alpha\beta}^n$:

$$(-n\omega + q_\beta) F_{\alpha\beta}^n = \sum_\gamma \sum_k \mathcal{H}_{\alpha\gamma}^{n-k} F_{\gamma\beta}^k$$

These equations can be rewritten in the form of a matrix eigenvalue equation:

$$\sum_{\gamma k} (\mathcal{H}_{\alpha\gamma}^{n-k} + n\omega \delta_{\alpha\gamma} \delta_{kn}) F_{\gamma\beta}^k = q_\beta F_{\alpha\beta}^n \quad (21)$$

In this equation q_β is the eigenvalue and $F_{\alpha\beta}^n$ is the corresponding eigenvector with components denoted by the pair of indices α, n . The operator is a matrix with rows identified by α, n and columns by γ, k . This operator will be denoted by \mathcal{H}_F and called the Floquet Hamiltonian associated with the semi-classical Hamiltonian \mathcal{H}_C . Since n and k range from $-\infty$ to $+\infty$, \mathcal{H}_F is an infinite matrix. We shall order the components so that α runs over the finite number of atomic states before each change in n . In the case of equations 1, for example, the Floquet Hamiltonian is:

$$\begin{pmatrix}
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
 \cdot & E_a - \omega & 0 & 0 & c & 0 & 0 & 0 & 0 & \cdot \\
 \cdot & 0 & E_\beta - \omega & c & 0 & 0 & 0 & 0 & 0 & \cdot \\
 \cdot & 0 & c & E_a & 0 & 0 & c & 0 & 0 & \cdot \\
 \cdot & c & 0 & 0 & E_\beta & c & 0 & 0 & 0 & \cdot \\
 \cdot & 0 & 0 & 0 & c & E_a + \omega & 0 & 0 & c & \cdot \\
 \cdot & 0 & 0 & c & 0 & 0 & E_\beta + \omega & c & 0 & \cdot \\
 \cdot & 0 & 0 & 0 & 0 & 0 & c & E_a + 2\omega & 0 & \cdot \\
 \cdot & 0 & 0 & 0 & 0 & c & 0 & 0 & E_\beta + 2\omega & \cdot \\
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
 \end{pmatrix} \quad (22)$$

Since two indices are required to identify a row or column of the matrix, it is convenient to introduce Dirac notation for the components of \mathcal{H}_F and F . Therefore let \mathcal{H}_F be defined by

$$\langle a n | \mathcal{H}_F | \beta m \rangle = \mathcal{H}_{a\beta}^{n-m} + n\omega \delta_{a\beta} \delta_{nm} \quad (23)$$

The $|a n \rangle$ are an orthonormal basis providing the above matrix representation of \mathcal{H}_F . They can be thought of as column matrices of all zeros, except for a one in the a, n position. Alternatively they can be thought of abstractly as elements of a Hilbert space with norm one. They are not actual quantum-mechanical states of a physical system, although they have similar properties.

The eigenvalues and normalized eigenvectors of \mathcal{H}_F will be denoted by $\lambda_{\beta m}$ and $|\lambda_{\beta m} \rangle$ respectively:

$$\mathcal{H}_F |\lambda_{\beta m} \rangle = \lambda_{\beta m} |\lambda_{\beta m} \rangle$$

If we take the inner product of both sides of this equation with $\langle a_n |$ and introduce the unit operator in the form $\sum_{\gamma k} |\gamma k\rangle \langle \gamma k|$ to the right of \mathcal{H}_F , we obtain the component form of the eigenvalue equation analogous to equation 21:

$$\sum_{\gamma k} \langle a_n | \mathcal{H}_F | \gamma k \rangle \langle \gamma k | \lambda_{\beta m} \rangle = \lambda_{\beta m} \langle a_n | \lambda_{\beta m} \rangle$$

Before we can identify the components of F with these eigenvectors, we must develop some of the properties of \mathcal{H}_F .

As can be seen from equation 23, \mathcal{H}_F has a periodic structure, with only the number of ω 's varying from block to block. From the definition this periodicity property can be written explicitly as

$$\langle a_{n+p} | \mathcal{H}_F | \beta_{m+p} \rangle = \langle a_n | \mathcal{H}_F | \beta_m \rangle + p\omega \delta_{a\beta} \delta_{nm}$$

This relation endows the eigenvalues and eigenvectors of \mathcal{H}_F with special properties. The eigenvalues are in principle found from the secular equation $\det(\mathcal{H}_F - \lambda \mathbb{1}) = 0$. If λ is replaced by $\lambda + p\omega$, the determinant is still the same. Hence if λ is an eigenvalue, so also is $\lambda + p\omega$ for any integer p . This property can also be seen in the Floquet solution, since by redefining the summation index n we can tack onto q any number of ω 's. To be precise we shall write

$\lambda_{an} = q_a + n\omega$, where $q_a = \lambda_{a0}$ is defined to be that member of the set having the smallest absolute value.

The eigenvector components $\langle a_n | \lambda_{\beta m} \rangle$ belonging to the eigenvalue $\lambda_{\beta m}$ are also related to each other by a simple shifting in m and n . The eigenvector $|\lambda_{\beta m+p}\rangle$ obeys

$$\mathcal{H}_F |\lambda_{\beta m+p} \rangle = \lambda_{\beta m+p} |\lambda_{\beta m+p} \rangle$$

Take the inner product of each side with $\langle a n+p |$ and introduce the unit operator $\sum_{\gamma k} |\gamma k+p \rangle \langle \gamma k+p |$ to the right of \mathcal{H}_F :

$$\begin{aligned} \sum_{\gamma k} \langle a n+p | \mathcal{H}_F |\gamma k+p \rangle \langle \gamma k+p | \lambda_{\beta m+p} \rangle \\ = \lambda_{\beta m+p} \langle a n+p | \lambda_{\beta m+p} \rangle \end{aligned}$$

Apply the periodicity properties of \mathcal{H}_F and $\lambda_{\beta m}$:

$$\begin{aligned} \sum_{\gamma k} [\langle a n | \mathcal{H}_F |\gamma k \rangle + p\omega \delta_{a\gamma} \delta_{nk}] \langle \gamma k+p | \lambda_{\beta m+p} \rangle \\ = (\lambda_{\beta m+p} + p\omega) \langle a n+p | \lambda_{\beta m+p} \rangle \end{aligned}$$

The $p\omega$ terms on each side cancel, leaving

$$\sum_{\gamma k} \langle a n | \mathcal{H}_F |\gamma k \rangle \langle \gamma k+p | \lambda_{\beta m+p} \rangle = \lambda_{\beta m} \langle a n+p | \lambda_{\beta m+p} \rangle$$

which is just the equation satisfied by $\langle a n | \lambda_{\beta m} \rangle$. Since they satisfy the same homogeneous equations, are both normalized, and have relative phases which we are free to choose, we can identify the components completely:

$$\langle a n+p | \lambda_{\beta m+p} \rangle = \langle a n | \lambda_{\beta m} \rangle \quad (24)$$

This relation will be used repeatedly in what follows.

Since both $F_{a\beta}^n$ and $\langle a n | \lambda_{\beta m} \rangle$ are eigenvectors of \mathcal{H}_F with the same eigenvalue $q_\beta = \lambda_{\beta 0}$, they must be proportional:

$$F_{\alpha\beta}^n = C_{\beta} \langle \alpha n | \lambda_{\beta 0} \rangle \quad (25)$$

We can evaluate C_{β} with the aid of equation 24. The matrix F is unitary: $F^{\dagger}F = 1$. In component notation this becomes

$$\sum_{\gamma} F_{\gamma\alpha}^*(t) F_{\gamma\beta}(t) = \delta_{\alpha\beta}$$

or

$$\sum_{\gamma} \left(\sum_m F_{\gamma\alpha}^{m*} e^{-im\omega t} e^{iq_{\alpha}t} \right) \left(\sum_n F_{\gamma\beta}^n e^{in\omega t} e^{-iq_{\beta}t} \right) = \delta_{\alpha\beta}$$

Because of the $\delta_{\alpha\beta}$ on the right, $e^{+i(q_{\alpha}-q_{\beta})t}$ can be set equal to one.

We replace the sum over m by a sum over $l = n - m$:

$$\sum_{\gamma} \sum_n \sum_l F_{\gamma\alpha}^{n-l*} F_{\gamma\beta}^n e^{il\omega t} = \delta_{\alpha\beta}$$

Since the right-hand side is independent of time, the left-hand side must be also:

$$\sum_{\gamma} \sum_n F_{\gamma\alpha}^{n-l*} F_{\gamma\beta}^n = \delta_{\alpha\beta} \delta_{l0}$$

Introduce equation 25 for the F 's:

$$\sum_{\gamma} \sum_n \langle \lambda_{\alpha 0} | \gamma n - l \rangle C_{\alpha}^* C_{\beta} \langle \gamma n | \lambda_{\beta 0} \rangle = \delta_{\alpha\beta} \delta_{l0}$$

We now use equation 24 to move l to the other side of the bracket:

$$\sum_{\gamma n} \langle \lambda_{\alpha l} | \gamma n \rangle \langle \gamma n | \lambda_{\beta 0} \rangle |C_{\beta}|^2 = \delta_{\alpha\beta} \delta_{l0}$$

The sum over γ and n produces the unit operator

$$\langle \lambda_{\alpha l} | \lambda_{\beta 0} \rangle |C_{\beta}|^2 = \delta_{\alpha\beta} \delta_{l0}$$

But the eigenvectors $|\lambda_{\beta m}\rangle$ are orthonormal. So we obtain finally $|C_{\beta}|^2 = 1$. Choosing the arbitrary phase to be zero, C_{β} equals one and equation 25 becomes

$$F_{\alpha\beta}^n = \langle \alpha n | \lambda_{\beta 0} \rangle$$

We have now completely reduced the problem of finding the unitary Floquet solution $F(t)$ of equation 18 to that of finding the eigenvalues and eigenvectors of the infinite matrix \mathcal{H}_F .

Let us also evaluate the components of $U(t; t_0) = F(t)F^{-1}(t_0)$ in Dirac notation:

$$U_{\beta\alpha}(t; t_0) = \sum_{\gamma} \sum_k \langle \beta k | \lambda_{\gamma 0} \rangle e^{ik\omega t} e^{-iq_{\gamma} t} \sum_{\ell} \langle \lambda_{\gamma 0} | \alpha - \ell \rangle e^{i\ell\omega t_0} e^{iq_{\gamma} t_0}$$

$-i(-\ell)\omega t_0$

We apply equation 24 to express both brackets in terms of $|\lambda_{\gamma\ell}\rangle$ and replace the summation index k by $n = k + \ell$:

$$U_{\beta\alpha}(t; t_0) = \sum_n \sum_{\gamma\ell} \langle \beta n | \lambda_{\gamma\ell} \rangle e^{-i\lambda_{\gamma\ell}(t-t_0)} \langle \lambda_{\gamma\ell} | \alpha 0 \rangle e^{in\omega t}$$

The sum over γ and ℓ produces the same function of \mathcal{H}_F as the function of $\lambda_{\gamma\ell}$ appearing between the ket and bra:

$$U_{\beta\alpha}(t; t_0) = \sum_n \langle \beta n | e^{-i\mathcal{H}_F(t-t_0)} | \alpha 0 \rangle e^{in\omega t} \quad (26)$$

The matrix elements appearing in this equation are the components of a vector $|t\rangle$, which satisfies the Schrödinger equation $i\frac{d}{dt}|t\rangle = \mathcal{H}_F|t\rangle$ with the initial condition $|t_0\rangle = |a0\rangle$. Thus $U_{\beta a}(t;t_0)$, which is the amplitude that a system initially in atomic state a at time t_0 evolve to state β by time t according to the time-dependent Hamiltonian $\mathcal{H}_C(t)$, can also be interpreted as the amplitude that a system initially in state $|a0\rangle$ at time t_0 evolve to state $|\beta n\rangle$ by time t according to the time-independent Hamiltonian \mathcal{H}_F , summed over n with weighting factors $e^{in\omega t}$. In so saying we imply that $|an\rangle$ and $|\beta m\rangle$ represent states of a quantum system. Now a and β do represent atomic states, but what are m and n states of, the oscillating field? In \mathcal{H}_C the field was considered classically. Is applying Floquet's theorem somehow related to quantizing the field? In chapter X we shall investigate this question, and find that it is indeed reasonable to associate $|an\rangle$ with quantum states of the oscillating field. In the meantime we shall refer to $|an\rangle$, etc. as "Floquet states" and give an interpretation of our equations as if they were actual quantum states. Our results will, of course, be independent of whether the reader regards them as physical states, or merely notational devices.

Now let us study the transition probabilities in Dirac notation. The transition probability from state a at time t_0 to state β at time t is:

$$P_{\beta \leftarrow a}(t;t_0) = |U_{\beta a}(t;t_0)|^2$$

$$= \sum_{km} \langle \beta k | e^{-i\mathcal{H}_F(t-t_0)} | a0 \rangle e^{im\omega t_0} \langle am | e^{+i\mathcal{H}_F(t-t_0)} | \beta k \rangle \quad (27)$$

If we let $|t_o\rangle = \sum_n A_n e^{-in\omega t_o} |an\rangle$, then

$$\begin{aligned} |t_o\rangle \langle t_o| &= \sum_{nk} A_n A_k^* e^{i(k-n)\omega t_o} |an\rangle \langle ak| \\ &= \sum_m |a0\rangle e^{im\omega t_o} \langle am| \end{aligned}$$

with $\sum_n A_n A_{n+m}^* = 1$. We can now write

$$P_{\beta \leftarrow a}(t; t_o) = \sum_k |\langle \beta k | e^{-i \mathcal{H}_F(t-t_o)} |t_o\rangle|^2 \quad (28)$$

and read it simply as the probability to go from an initial state $|t_o\rangle$, which is atomic state a and a coherent field state, to a final atomic state β , summed over all possible final field states.

It is usually necessary to average the transition probability over the initial time t_o , keeping the elapsed time $t - t_o$ fixed, in order to compare the theory with experiment. The reason for doing this in the case of atomic beam experiments was mentioned at the beginning of this chapter. In other kinds of experiments the initial time is often determined by the action of a relaxation process on the atom, and thus would again be randomly distributed in time compared to the phase of the oscillating field. This average is readily performed on equation 27, yielding

$$P_{\beta \leftarrow a}(t - t_o) = \sum_k |\langle \beta k | e^{-i \mathcal{H}_F(t-t_o)} |a0\rangle|^2 \quad (29)$$

This differs from equation 28 only in the initial state. In equation 28 we

had a coherent mixture for an initial state, presumably describing a field of well defined phase. In equation 29 our initial state is a pure Floquet state, and must presumably describe a field with undefined phase. As can be readily verified from the periodicity properties, it does not matter whether the initial state in equation 29 is $|a_0\rangle$ or $|a_m\rangle$, so long as it is pure.

If we also average over $t - t_0$ we obtain the all time average transition probability:

$$\bar{P}_{\beta \leftarrow a} = \sum_k \sum_{\gamma \ell} |\langle \beta k | \lambda_{\gamma \ell} \rangle \langle \lambda_{\gamma \ell} | a_0 \rangle|^2 = \sum_{\gamma} T_{\beta \gamma} T_{a \gamma} \quad (30)$$

where the N by N matrix T is defined to be a partial sum of the squares of the eigenvector components:

$$T_{a\beta} = \sum_{\ell} |\langle a \ell | \lambda_{\beta 0} \rangle|^2 = \sum_m |\langle a_0 | \lambda_{\beta m} \rangle|^2 \quad (31)$$

If all non-zero differences $\lambda_{\gamma \ell} - \lambda_{\delta m}$ are large compared to $1/\tau$, where τ is either $t - t_0$, or a relaxation time, whichever is smaller, then \bar{P} is the transition probability we want to compare with experiment.

Regardless of the physical interpretation, equations 29 and 30 provide a method of computing time average transition probabilities which is much superior to previous methods that require a complete evaluation of $U_{\beta a}(t; t_0)$, squaring, and finally averaging away half of the laboriously computed terms. Equation 29 merely says that we compute the transition probability from a single Floquet state $|a_0\rangle$ to various states $|\beta k\rangle$ as governed by the time-independent Hamiltonian \mathcal{H}_F .

Since these probabilities decrease rapidly as k departs from 0, only a very few terms in the infinite sum over k need be calculated. We have, in effect, by introducing \mathcal{H}_F , transformed the time-dependent problem to a many-level problem with constant Hamiltonian subject to the methods of chapters IV and V.

In addition to transition probabilities we can compute all of the elements of the density matrix for the atomic states as a function of time from the density matrix at any given time:

$$\rho(t) = U(t;t_0)\rho(t_0)U^{-1}(t;t_0)$$

We can then find the expectation value of any atomic operator as a function of time by the usual rule of quantum statistical mechanics. When ρ is expanded in terms of Floquet states it becomes a sum of terms oscillating with frequencies corresponding to the differences between two of the eigenvalues of the Floquet Hamiltonian. This is the general time dependence of the expectation value of any atomic operator.

In many cases, such as a gas at low pressure, we observe an expectation value averaged over initial (collision) times t_0 keeping laboratory time t fixed, and the initial value of ρ would be constant, representing some sort of thermal equilibrium. Under this kind of average the time dependence of the expectation value contains only the exciting frequency and its harmonics and does not contain any q 's. If we compute the expectation value of an electric or magnetic moment, then following the semi-classical theory of radiation we can use these oscillating moments as classical sources to find the spontaneous radiation emitted by the atom at harmonic frequencies. This procedure was

used by Armstrong et al. (36) to predict the existence of optical harmonic generation in matter. They used the solutions of time-dependent perturbation theory, but the formalism of this chapter is exact, provided only that eigenvalues and eigenvectors of the Floquet Hamiltonian are found. In the following chapters we have concentrated on transition probabilities, leaving the large, interesting subject of harmonic generation for future exploration.

VII. IMPROVED PERTURBATION SOLUTIONS -- TWO LEVELS

We now turn to the solution of equations 1, utilizing the formal methods developed in chapter VI. In this chapter we shall apply the perturbation techniques introduced in chapter IV to the Floquet Hamiltonian and discover the basic resonance properties of a two state system. We shall use the phase factored form, equation 2, since it has a larger frequency. It is also traceless, so by equation 20 the characteristic exponents can be written $+q$ and $-q$. The Floquet Hamiltonian for equation 2 is

$$\begin{pmatrix}
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
 \cdot & -\Delta-2\omega & c & 0 & 0 & 0 & 0 & \cdot \\
 \cdot & c & \Delta-2\omega & c & 0 & 0 & 0 & \cdot \\
 \cdot & 0 & c & -\Delta & c & 0 & 0 & \cdot \\
 \cdot & 0 & 0 & c & \Delta & c & 0 & \cdot \\
 \cdot & 0 & 0 & 0 & c & -\Delta+2\omega & c & \cdot \\
 \cdot & 0 & 0 & 0 & 0 & c & \Delta+2\omega & \cdot \\
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
 \end{pmatrix}
 \begin{matrix}
 \cdot & \cdot \\
 \alpha & -1 \\
 \beta & -1 \\
 \alpha & 0 \\
 \beta & 0 \\
 \alpha & 1 \\
 \beta & 1 \\
 \cdot & \cdot
 \end{matrix}
 \quad (32)$$

where $\Delta = \frac{1}{2}(\omega - \omega_0)$. The row indices are given at the right to help identify the components.

If the Floquet Hamiltonian for equation 1, shown in equation 22, is examined closely, it will be discerned that E_β is coupled through c to $E_\alpha \pm \omega$, and indirectly to $E_\alpha \pm 3\omega$, $E_\beta \pm 2\omega$, \dots , but not at all to E_α , $E_\beta \pm \omega$, \dots . The whole system of equations can be separated into

two independent sets of equations; the sets differ only by one ω in energy scale. The phase factoring transformation has shifted these two sets so they coincide with each other, giving us a simpler \mathcal{H}_F to work with. This phenomenon will always occur when the phase factoring described in chapter IV produces a Hamiltonian of frequency 2ω instead of ω .

Let us first investigate the transition probabilities near the primary resonance $\omega \approx \omega_0$, using equation 29. The Floquet states $|\alpha 0\rangle$ and $|\beta 0\rangle$ are nearly degenerate, while all other states are relatively far away. If we simply neglect all other states, we are making the rotating field approximation discussed in chapter III. The rotating field solution will be called the zeroth order solution to equations 1 near resonance. Considering c , Δ , and q of the same order we seek solutions to higher orders in c/ω .

To get a first order solution we merely treat the other states by the degenerate perturbation theory of Appendix A, obtaining the two level matrix

$$\begin{pmatrix} -\Delta + \frac{c^2}{2\omega} & c \\ c & \Delta - \frac{c^2}{2\omega} \end{pmatrix}$$

(We have neglected q and Δ compared to ω in the denominator.) As in chapter IV the first order solution is then given by equation 7 with $n = 1$, $\omega_{\text{res}} = \omega_0 + \frac{c^2}{\omega}$, and $u = 2c$. This is the Bloch-Siegert solution.

The first order solution was so easy, we ought to work out the second order. To do this we shall evaluate the eigenvalues and eigenvectors of \mathcal{H}_F carefully, illustrating explicitly the use of our theory.

We determine the eigenvalues from equation A8 of Appendix A. The only change from first order to second is to retain q and Δ in the denominators of the c^2 terms. We then expand these terms on the basis of $q, \Delta \ll \omega$:

$$\frac{c^2}{q \mp \Delta \pm 2\omega} \approx \pm \frac{c^2}{2\omega} \left(1 + \frac{\Delta}{2\omega} \mp \frac{q}{2\omega} \right)$$

If we define $\Delta' = \Delta - \frac{c^2}{2\omega} - \frac{\Delta c^2}{4\omega^2} \approx (\Delta - \frac{c^2}{2\omega})(1 - \frac{c^2}{4\omega^2})$, our two by two matrix becomes:

$$\begin{pmatrix} -\Delta' - \frac{c^2 q}{4\omega^2} & c \\ c & \Delta' - \frac{c^2 q}{4\omega^2} \end{pmatrix}$$

Its eigenvalues are $q = -\frac{c^2 q}{4\omega^2} \pm p$, where $p = (c^2 + \Delta'^2)^{1/2}$. Solving for q : $q \approx (1 - \frac{c^2}{4\omega^2})p$. In detail we have

$$q^2 = c^2 \left(1 - \frac{c^2}{4\omega^2}\right)^2 + \left(\Delta - \frac{c^2}{2\omega}\right)^2 \left(1 - \frac{c^2}{2\omega^2}\right)^2 + \text{order } \frac{c^5}{\omega^3} \quad (33)$$

We see that q is still a hyperbolic function of Δ , as it was in lower orders of approximation. In terms of this q the eigenvalues of \mathcal{H}_F are

$$\begin{aligned} \lambda_{\alpha n} &= q + 2n\omega \\ \lambda_{\beta n} &= -q + 2n\omega \end{aligned} \quad (34)$$

The eigenvector components for the two by two matrix are found from equation A10:

$$\begin{aligned}
 \langle \alpha 0 | \lambda_{\alpha 0} \rangle &= N \left(\frac{p - \Delta'}{2p} \right)^{1/2} = - \langle \beta 0 | \lambda_{\beta 0} \rangle \\
 \langle \beta 0 | \lambda_{\alpha 0} \rangle &= N \left(\frac{p + \Delta'}{2p} \right)^{1/2} = \langle \alpha 0 | \lambda_{\beta 0} \rangle
 \end{aligned} \tag{35}$$

where N is a normalization constant approximately equal to one. From equation A6 of perturbation theory, the other components can be expressed in terms of these:

$$\begin{aligned}
 \langle \alpha 1 | \lambda_{\alpha 0} \rangle &= \frac{c}{q + \Delta - 2\omega} \langle \beta 0 | \lambda_{\alpha 0} \rangle \approx \frac{-c}{2\omega} \left(\frac{p + \Delta'}{2p} \right)^{1/2} \\
 \langle \beta -1 | \lambda_{\alpha 0} \rangle &= \frac{c}{q - \Delta + 2\omega} \langle \alpha 0 | \lambda_{\alpha 0} \rangle \approx \frac{c}{2\omega} \left(\frac{p - \Delta'}{2p} \right)^{1/2} \\
 \langle \alpha 1 | \lambda_{\beta 0} \rangle &= \frac{c}{-q + \Delta - 2\omega} \langle \beta 0 | \lambda_{\beta 0} \rangle \approx \frac{c}{2\omega} \left(\frac{p - \Delta'}{2p} \right)^{1/2} \\
 \langle \beta -1 | \lambda_{\beta 0} \rangle &= \frac{c}{-q - \Delta + 2\omega} \langle \alpha 0 | \lambda_{\beta 0} \rangle \approx \frac{c}{2\omega} \left(\frac{p + \Delta'}{2p} \right)^{1/2}
 \end{aligned} \tag{35}$$

All others are of higher order and will not be needed. The normalization is

$$|\langle \alpha 1 | \lambda_{\alpha 0} \rangle|^2 + |\langle \alpha 0 | \lambda_{\alpha 0} \rangle|^2 + |\langle \beta 0 | \lambda_{\alpha 0} \rangle|^2 + |\langle \beta -1 | \lambda_{\alpha 0} \rangle|^2 = 1$$

giving $N \approx 1 - \frac{c^2}{8\omega^2}$.

To compute the matrix elements of $\exp(-i \mathcal{H}_F t)$ we use the expansion in terms of the eigenvectors of \mathcal{H}_F :

$$\langle \beta k | e^{-i \mathcal{H}_F t} | \alpha 0 \rangle = \sum_{\gamma n} \langle \beta k | \lambda_{\gamma n} \rangle e^{-i \lambda_{\gamma n} t} \langle \lambda_{\gamma n} | \alpha 0 \rangle$$

For $k = 0$ we have two terms:

$$\begin{aligned} \langle \beta 0 | e^{-i \mathcal{H}_F t} | \alpha 0 \rangle &= \langle \beta 0 | \lambda_{\alpha 0} \rangle e^{-i \lambda_{\alpha 0} t} \langle \lambda_{\alpha 0} | \alpha 0 \rangle \\ &+ \langle \beta 0 | \lambda_{\beta 0} \rangle e^{-i \lambda_{\beta 0} t} \langle \lambda_{\beta 0} | \alpha 0 \rangle \end{aligned}$$

The other terms in the sum are of third order or higher. With the eigenvalues and eigenvectors just computed this reduces to

$$\langle \beta 0 | e^{-i \mathcal{H}_F t} | \alpha 0 \rangle = -i \frac{c}{p} \left(1 - \frac{c^2}{4\omega^2} \right) \sin qt$$

For $k = 1$ or -2 we have only terms of second order and higher. When squared these give fourth order terms, which we are neglecting. For $k = -1$ we have four terms of first order, corresponding to the γ_n values: $\alpha 0$, $\beta 0$, $\alpha -1$, $\beta -1$. Using equation 24 all components can be changed to those given in equations 35, giving us

$$\begin{aligned} \frac{c}{2\omega} \frac{p - \Delta'}{2p} e^{-iqt} + \frac{c}{2\omega} \frac{p + \Delta'}{2p} e^{iqt} - \frac{c}{2\omega} \frac{p + \Delta'}{2p} e^{-iqt} e^{2i\omega t} \\ - \frac{c}{2\omega} \frac{p - \Delta'}{2p} e^{iqt} e^{2i\omega t} \end{aligned}$$

This can be rewritten as

$$\frac{c}{2\omega} \left[(\cos qt + i \frac{\Delta'}{p} \sin qt) - (\cos qt - i \frac{\Delta'}{p} \sin qt) e^{2i\omega t} \right]$$

Now we are ready to evaluate the transition probability by equation 29:

$$\begin{aligned} P_{\beta \leftarrow \alpha}(t) &= |\langle \beta 0 | e^{-i \mathcal{H}_F t} | \alpha 0 \rangle|^2 + |\langle \beta -1 | e^{-i \mathcal{H}_F t} | \alpha 0 \rangle|^2 + O\left(\frac{c}{\omega}\right)^4 \\ &= \frac{c^2}{p^2} \left(1 - \frac{c^2}{4\omega^2} \right)^2 \sin^2 qt + \frac{c^2}{4\omega^2} \left[2 \cos^2 qt + 2 \frac{\Delta'^2}{p^2} \sin^2 qt \right. \\ &\quad \left. - 2 \cos^2 qt \cos 2\omega t + \frac{2\Delta'^2}{p^2} \sin^2 qt \cos 2\omega t \right. \\ &\quad \left. - \frac{4\Delta'}{p} \sin qt \cos qt \sin 2\omega t \right] \end{aligned}$$

Rearranging some of the trig functions we get finally

$$P_{\beta \leftarrow \alpha}(t) = \frac{c^2}{p^2} \left(1 - \frac{c^2}{\omega^2}\right) \sin^2 qt + \frac{c^2}{2\omega^2} \\ - \frac{c^2}{4\omega^2} \left[\left(\frac{c^2}{p^2} + \frac{p^2 + \Delta'^2}{p^2} \cos 2qt \right) \cos 2\omega t + 2 \frac{\Delta'}{p} \sin 2qt \sin 2\omega t \right] \quad (36)$$

We should remember that this is the transition probability averaged over initial times. The transition probability with the initial-time dependence included (equation 27) contains many more terms. The use of equation 29 has saved us the trouble of computing these extra terms which we do not observe experimentally.

When $\frac{c}{\omega}$ is small and we are close to resonance, the second line of equation 36 oscillates very rapidly compared to the first line and may be disregarded as not observed. The remainder is of the Rabi form, except for a small decrease in amplitude and the addition of a constant term, representing the off-resonance background transition probability. Such effects are usually created by experimental conditions anyway. The line shape retains symmetry with respect to ω_0 , but not with respect to ω .

In sum we find in equation 36 that the modifications produced in the Rabi line shape (equation 3) by the presence of \mathcal{H}_1 in equation 2 are a shift in the resonance peak, a reduction in amplitude and the addition of a base. These modifications do not destroy the basic features of the line shape. Similar types of modifications due to oscillatory, nonresonant perturbations can be expected in all resonance transitions. Henceforth we can utilize the Rabi-type line shapes found from chapter IV,

equation 7 with increased confidence of their validity, even when $\frac{c}{\omega}$ is as large as $\frac{1}{4}$.

In chapter II third order time-dependent perturbation theory suggested that there be a resonance at $3\omega = \omega_o + \frac{9c^2}{2\omega_o}$. We now have the tools necessary to study this possibility. Δ will no longer be a useful parameter, so we replace it by $\frac{1}{2}(\omega - \omega_o)$. Then the diagonal elements of \mathcal{H}_F contain a succession of half integral numbers of ω 's plus or minus $\frac{1}{2}\omega_o$. Looking through \mathcal{H}_F we find that when $3\omega \approx \omega_o$, $|a0\rangle$ is approximately degenerate with $|\beta 1\rangle$. Applying the perturbation theory with these two states treated as degenerate and setting $\omega_o = 3\omega$ in the denominators of the perturbation corrections we obtain the two by two matrix

$$\begin{pmatrix} -\frac{1}{2}\omega + \frac{1}{2}\omega_o + \frac{3c^2}{4\omega} & -\frac{c^3}{4\omega^2} \\ -\frac{c^3}{4\omega^2} & \frac{5\omega}{2} - \frac{1}{2}\omega_o - \frac{3c^2}{4\omega} \end{pmatrix}$$

The transition probability $|\langle \beta 1 | e^{-i\mathcal{H}_F t} | a0 \rangle|^2$ is then of the Rabi type given by equation 7 with $n = 3$,

$$\omega_{\text{res}} = \omega_o + \frac{3c^2}{2\omega} \text{ or } \omega_o + \frac{9c^2}{2\omega_o} \text{ and } u = \frac{c^3}{2\omega^2} \text{ or } \frac{9c^3}{2\omega_o^2}$$

The other terms in the sum in equation 29 are of order $(c/\omega)^2$. So there is indeed a resonance, corresponding to a triple quantum transition. Note that there is a frequency shift analogous to the Bloch-Siegert shift, but that it is greater than the line width, and is thus very

important for experimental observation. The Rabi-type formula for this transition has been previously derived by Winter (21). His results agree with ours in frequency shift, but disagree by a factor of two in the line width. Autler and Townes (1) were apparently unaware of this resonance, although their numerical results revealed it.

Strong fields are required to observe this transition, because if the line width is much less than the experimental resolution, it cannot be seen. For example in a typical atomic beam experiment a transition at 10^{10} cps might be optimally excited ($2c \approx \pi/t$) by about one milliwatt of microwave power input to a resonant cavity, giving a line width of about 10^4 cps. At this low power level the Bloch-Siegert shift would be only 10^{-3} cps and the three quantum resonance would have a line width of the order of 10^{-9} cps, neither of which is anywhere near observable. In order to excite the three quantum resonance optimally ($c^3/2\omega^2 \approx \pi/t$) we would have to supply 100 kilowatts of input power at $1/3 \times 10^{10}$ cps, assuming a resonant cavity with the same Q . We would then have a line width of $1/3 \times 10^4$ cps (we are assuming t is the same in both cases), and the peak frequency would be shifted 375 kilocycles from $1/3 \times 10^{10}$ or 333 megacycles.

The three-quantum transition can be thought of as a result of the alternate actions of the rotating and anti-rotating components of the oscillating field. For our physical example of an electron in a magnetic field we can describe it as follows. With the electron initially in the lower state $m = -1/2$, it first absorbs a photon from the rotating ($M_z = +1$) component of the field, going to the upper state $m = 1/2$ with non-conservation of energy. It cannot absorb another rotating photon because of

angular momentum limitations, but it can absorb an antirotating ($M_z = -1$) photon to return virtually to state $m = -1/2$, but adding energy. Finally it absorbs another rotating ($M_z = +1$) photon to arrive in the $m = 1/2$ state with energy and angular momentum conservation. Marjorie and Brossel (4) show this pictorially, except their figure implies that the photons are absorbed in a different order. Since the energy nonconserving intermediate states have very short lifetimes, a very high photon density is required to get all three photons in before the system decays back into the initial state. The classical solution of this problem will also show this resonance.

One might next inquire if there are other multiple quantum transitions for the two state system. The unperturbed energy associated with $|\alpha 0\rangle$ is $-\frac{1}{2}\omega + \frac{1}{2}\omega_0$, and with $|\beta p\rangle$, $(2p + \frac{1}{2})\omega - \frac{1}{2}\omega_0$. These are approximately degenerate for $(2p + 1)\omega = \omega_0$. Thus multiple quantum transitions should occur for ω_0 equal to any odd harmonic of the driving frequency. They do not occur at even harmonics, because our perturbation has only off diagonal elements with respect to the atomic states. In the case of the electron in a magnetic field this selection rule can also be understood from the conservation of the z component of angular momentum.

We have already done the cases $p = 0$ and 1 in this chapter. To the same approximation we can just as easily find the Rabi-type solutions for any value of p . The result is equation 7 with

$$\begin{aligned}
 n &= 2p + 1 \\
 \omega_{\text{res}} &= \omega_0 + \frac{2p+1}{p(p+1)} \frac{c^2}{\omega} \quad \text{or} \quad \omega_0 + \frac{(2p+1)^2}{p(p+1)} \frac{c^2}{\omega_0}, \quad p > 0 \quad (37) \\
 u &= \frac{c^{2p+1}}{2^{2p-1}(p!)^2 \omega^{2p}} \quad \text{or} \quad \frac{(2p+1)^{2p}}{2^{2p-1}(p!)^2} \frac{c^{2p+1}}{\omega_0^{2p}} \quad p \geq 0
 \end{aligned}$$

These results were also found by Winter (21), except that he did not know the numerical factors in the u 's.

Keeping c and ω fixed and looking at the transition probability as a function of ω_0 , equation 37 says we should find resonances near $\omega_0 = \omega, 3\omega, 5\omega, 7\omega, \dots$. The shifts are all towards smaller ω_0 and decrease with increasing p (compare figure 6b). The widths decrease rapidly, because of the powers of c/ω . However even if c/ω were large, the widths would eventually decrease because of the factorials in the denominator. So only a finite number of resonances would have sufficient width to be observable.

Keeping c and ω_0 fixed and looking at the transition probability as a function of ω , equation 37 says we should find resonances near $\omega = \omega_0, \omega_0/3, \omega_0/5, \dots$. The shifts are all towards larger ω (compare figure 10). The widths decrease as p increases only when c/ω_0 is small. The transition probability is probably simpler as a function of ω_0 , than as a function of ω . In magnetic resonance experiments it is usually measured as a function of ω_0 by varying the static magnetic field.

VIII. THE CHARACTERISTIC EXPONENT STRONG FIELD SOLUTION FOR TWO STATES

The procedure for solving equations 1, as developed in chapter VI and illustrated in chapter VII, is to write down the Floquet Hamiltonian, determine its eigenvalues or the characteristic exponents, determine the corresponding eigenvectors, and then substitute into one of the equations 26, 28, 29, or 30. The most important and most difficult step is the evaluation of the characteristic exponent.

It was pointed out by Autler and Townes (1) that when we have two isolated states α and β subject to a strong oscillating field at frequency ω and then observe a very weakly excited transition between this pair and a third far removed state γ , resonance in the latter transition occurs when the frequency of the weak excitation $\omega^{\dagger} = E_{\gamma} - q_{\alpha} - n\omega$ or $E_{\gamma} - q_{\beta} - n\omega$, where $q_{\alpha} + n\omega$ and $q_{\beta} + n\omega$ are the characteristic exponents for the α, β system or the frequencies of the components of the U matrix. Hence the values of the characteristic exponents are experimentally observable quantities.

Since the characteristic exponents are the eigenvalues of a many-level system, we can plot them as functions of a parameter and analyze the graph for resonances according to the discussion in chapter V. Autler and Townes (1) made such a plot of the characteristic exponents for equations 1 as a function of ω . We shall instead look at the characteristic exponents as a function of ω_0 keeping ω constant. By inspection of such a graph we then locate resonances and form a qualitative idea of the transition probabilities.

Because of the periodic properties of the eigenvectors of the Floquet Hamiltonian and the simplicity of only two atomic states in equations 1 we can actually find quantitative information about transition probabilities from a graph of the characteristic exponents. Let ω_0 correspond to the y parameter of chapter V. Then, referring to equation 32, all unperturbed Floquet states $|\alpha n\rangle$ have slope $a_\alpha = +\frac{1}{2}$, and all states $|\beta m\rangle$ have slope $a_\beta = -\frac{1}{2}$. From equation 13 we have

$$\frac{\partial \lambda_{\alpha 0}}{\partial y_0} = \frac{\partial q}{\partial \omega_0} = \sum_{\gamma \ell} a_\gamma \langle \gamma \ell | \lambda_{\alpha 0} \rangle^2$$

We have chosen the a 's to be independent of ℓ . We can thus perform the sum over ℓ and express the result in terms of the T matrix defined in equation 31:

$$\frac{\partial q}{\partial \omega_0} = \frac{1}{2} T_{\alpha\alpha} - \frac{1}{2} T_{\beta\alpha} \quad (38)$$

From the normalization of the eigenvectors we have

$$\sum_{\gamma} T_{\alpha\gamma} = \sum_{\gamma} T_{\beta\gamma} = \sum_{\gamma} T_{\gamma\alpha} = \sum_{\gamma} T_{\gamma\beta} = 1$$

These equations alone define all four components of T in terms of any one. The additional relation among the T 's found in equation 38 completes their determination:

$$T_{\alpha\alpha} = T_{\beta\beta} = \frac{1}{2} + \frac{\partial q}{\partial \omega_0}$$

$$T_{\alpha\beta} = T_{\beta\alpha} = \frac{1}{2} - \frac{\partial q}{\partial \omega_0}$$

We now substitute these into equation 30 and find for the all time average

transition probability

$$\overline{P}_{\beta \leftarrow \alpha} = \frac{1}{2} \left[1 - 4 \left(\frac{\partial q}{\partial \omega_0} \right)^2 \right] \quad (39)$$

This remarkable result permits us to sketch the time average transition probability directly from a plot of the characteristic exponent. In particular it tells us that resonance peaks occur at $\frac{\partial q}{\partial \omega_0} = 0$ and always have magnitude one half.

For the several reasons outlined above, a considerable effort was expended in determining the characteristic exponent for the simple two level problem as a function of the parameters c , ω , and ω_0 , using every conceivable line of attack. To keep the equations as concise as possible the work was done in a dimensionless notation, utilizing ω as a scale parameter. We define

$$\begin{aligned} x &= \frac{2c}{\omega} \\ y &= \frac{\omega_0}{\omega} \quad \text{or} \quad 1 - y = \frac{2\Delta}{\omega} \\ z &= \frac{2q}{\omega} \\ \tau &= \frac{\omega t}{2} \end{aligned} \quad (40)$$

In terms of this notation equation 2 becomes

$$i \frac{d}{d\tau} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} -1 + y & x(1 + e^{4i\tau}) \\ x(1 + e^{-4i\tau}) & 1 - y \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (41)$$

The Floquet Hamiltonian becomes

$$\begin{pmatrix}
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
 \cdot & -3-y & x & 0 & 0 & 0 & 0 & \cdot \\
 \cdot & x & -1+y & x & 0 & 0 & 0 & \cdot \\
 \cdot & 0 & x & 1-y & x & 0 & 0 & \cdot \\
 \cdot & 0 & 0 & x & 3+y & x & 0 & \cdot \\
 \cdot & 0 & 0 & 0 & x & 5-y & x & \cdot \\
 \cdot & 0 & 0 & 0 & 0 & x & 7+y & \cdot \\
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
 \end{pmatrix}
 \begin{matrix}
 \cdot & \cdot \\
 \beta & -1 \\
 \alpha & 0 \\
 \beta & 0 \\
 \alpha & 1 \\
 \beta & 1 \\
 \alpha & 2 \\
 \cdot & \cdot
 \end{matrix}
 \quad (42)$$

and equation 39 is

$$\overline{P}_{\beta \leftarrow \alpha} = \frac{1}{2} \left[1 - \left(\frac{\partial z}{\partial y} \right) \right]^2 \quad (43)$$

The characteristic exponent for the differential equation 41 is z . We wish to evaluate z as a function of the two parameters x and y . We shall first mention some general properties of $z(x, y)$ and then find approximations to it valid for various regions of x and y until we have a complete picture of its behavior. Then at the end of the chapter we shall interpret the results in terms of transition probabilities for the two state system excited by a strong oscillating field.

The Hamiltonian \mathcal{H}_C in equation 41 has frequency 4 (period $\pi/2$) and trace 0. Thus if z is a characteristic exponent, so also is $z + 4n$ and $-z + 4n$ for any integer n (compare equations 34). This multiple-valuedness must be remembered, since some of our approximations will jump from branch to branch.

The elements of \mathcal{H}_C are entire functions of x and y . Then, as shown by Moulton (35), any component $f(\tau)$ of the solution of the Schrödinger differential equation is also an entire function of x and y

at any value of τ . If we write $f(\tau) = e^{-iz\tau} \sum_n A_n e^{i4n\tau}$, then $f(\pi/2) = e^{-i\pi z/2} f(0)$ or $e^{-i\pi z/2}$ is an entire function of x and y . By writing differential equations for the real and imaginary parts of f separately we can similarly show that $\cos \pi z/2$ is an entire function of x and y . The multivaluedness of z comes entirely from the inverse cosine function.

In principle z is determined from the eigenvalue equation or infinite set of coupled recursion relations

$$(4n - 1 + y - z)A_n + xB_n + xB_{n-1} = 0 \quad (44)$$

$$(4n + 1 - y - z)B_n + xA_n + xA_{n+1} = 0$$

By juggling these equations one can determine the symmetry properties:

$$z(x, y) = z(-x, y) \quad (45)$$

$$z(x, y) - 1 = 1 - z(x, -y)$$

Hence it is sufficient to study z for positive x and y .

Since every Floquet state in equation 42 is connected to every other one by a unique chain of x 's and intermediate states, we expect the eigenvalues of \mathcal{H}_F to be nondegenerate for $x > 0$. A possible proof is to start with a two by two submatrix. By explicitly diagonalizing this we show it to be nondegenerate. We then add a third level. With the first two diagonal with respect to each other, their interaction with the third level is of the form of a perturbation due to a single level and leads to nondegeneracy for all three levels by an argument given in Condon and Shortley (37). This argument can be repeated, adding in one

level at a time, for any finite submatrix, and presumably by induction to the infinite matrix. Nondegeneracy in z means that z cannot be the same as any of its other branches, or that

$$z \neq 0, \pm 2, \pm 4, \dots \quad (46)$$

Thus in a plot of the multiple values of z , the lines $z = 0, \pm 2, \pm 4, \dots$ can never be crossed by z , or each branch of z is confined to a strip of height 2 (see figure 5).

When $x = 0$ the solutions of equations 41 are simple exponentials:

$$\alpha = C_{\alpha} e^{i(1-y)\tau} \quad \beta = C_{\beta} e^{-i(1-y)\tau}$$

Thus in the limit of x approaching zero we must have $z = \pm(1-y) + 4n$. Plotted as a function of y this represents an infinite grid of intersecting lines of slope $\pm y$, as in the right portion of figure 5. For $x > 0$ we have just seen that the z curves cannot cross, hence each intersection point must be replaced by a little hyperbola. Each branch of z is then continuous in y , and nearly a triangular wave of constant amplitude but slightly rounded corners. This is the very small x approximation.

We shall now consider an approximate solution for large values of y . It is obtained by the so-called adiabatic approximation in which we work with instantaneous eigenfunctions (compare reference 3, p. 213 f). We solve the eigenvalue equation

$$\mathcal{H}_C(\tau) S(\tau) = S(\tau) E(\tau)$$

at each instant of time τ . Since \mathcal{H}_C is periodic in τ , so also are S and E . Let us define a transformed solution W by

$$W(\tau) = S^{-1}(\tau) F(\tau)$$

where F is a solution of $i(d/d\tau)F = \mathcal{H}_C F$. Since S is periodic, W has the same characteristic exponent as F . W now obeys the Schrödinger type equation

$$i \frac{d}{d\tau} W = [E + i \left(\frac{d}{d\tau} S^{-1} \right) S] W$$

The adiabatic approximation consists of neglecting $(\frac{d}{d\tau} S^{-1})S$ relative to E . Since E is diagonal we then have the approximate solution

$$W(\tau) \approx W(0) \exp \left[-i \int_0^\tau E(\tau') d\tau' \right]$$

Let $E(\tau) = Q + \tilde{E}(\tau)$, where Q is the time average of E and \tilde{E} is the oscillating part. Then we can write W as

$$W(\tau) \approx W(0) \exp \left[-i \int_0^\tau \tilde{E}(\tau') d\tau' \right] e^{-iQ\tau}$$

which is just the Floquet form of solution. Hence the characteristic exponents for W or F are the elements of $Q = (2/\pi) \int_0^\pi E(\tau) d\tau$.

Using the \mathcal{H}_C of equation 41 we find

$$E(\tau) = \sigma_z [(1-y)^2 + 4x^2 \cos^2 2\tau]^{1/2}$$

The integral for the time average can be expressed in terms of a complete elliptic integral of the second kind. Our approximation for z is then

$$z \approx \frac{2}{\pi} [(1-y)^2 + 4x^2]^{1/2} E \left(\frac{2x}{[(1-y)^2 + 4x^2]^{1/2}} \right) = \frac{2}{\pi} (1-y) E \left(\frac{2ix}{1-y} \right) \quad (47)$$

The first form is useful for tabular evaluation of the elliptic integral,

while the second is useful with a power series approximation for it. By computing $(\frac{d}{d\tau} S^{-1})S$ and comparing with E we find that this approximation for z is valid when $y \gg 1$ and $y^2 \gg x$. Because of these restrictions an expansion of equation 47 in powers of x/y may be an equally good approximation:

$$z \approx 1 - y - \frac{x^2}{y} + \frac{3}{4} \frac{x^4}{y^3} \dots \quad (48)$$

In its region of validity this approximation is monotonic, hence it does not stay in a strip, but crosses from branch to branch of z .

Our next approximate evaluation of z will be for small values of y . To find such we want a differential equation with the y terms off diagonal and the x terms diagonal. This merely requires a change of dependent variable. Starting with equation 41 we first undo part of the phase factoring by defining $a(\tau) = e^{-i\tau} \alpha(\tau)$, $b(\tau) = e^{i\tau} \beta(\tau)$. Then a and b satisfy the differential equations

$$i \frac{da}{d\tau} = ya + (2x \cos 2\tau)b \quad (49)$$

$$i \frac{db}{d\tau} = (2x \cos 2\tau)a - yb$$

and have characteristic exponents $\pm (1 - z) + 2n$. Adding and subtracting these two equations we obtain

$$i \frac{d}{d\tau} (a + b) = 2x \cos 2\tau (a + b) + y(a - b)$$

$$i \frac{d}{d\tau} (a - b) = y(a + b) - 2x \cos 2\tau (a - b)$$

These equations become uncoupled for $y = 0$ and can be solved exactly,

yielding $a = \cos(x \sin 2\tau)$ and $b = -i \sin(x \sin 2\tau)$. We can proceed to find the effect on these solutions of a small y by a method similar to that slipped into chapter II.

Define: $a \pm b = u^\pm(\tau) e^{\mp i x \sin 2\tau} e^{i(z-1)\tau}$.

The u 's obey

$$i \frac{d}{d\tau} u^\pm = (z-1)u^\pm + y e^{\pm 2ix \sin 2\tau} u^\mp$$

For $y = 0$ we have $z = 1$ and $u^\pm = 1$. Using these as first approximations for u , and expanding the exponential in Fourier series

$$i \frac{d}{d\tau} u^\pm = (z-1) + y \sum_n J_n(2x) e^{\pm 2in\tau}$$

If $1-z$ is to be the characteristic exponent, u must be a periodic function of τ . The constant terms on the right will be proportional to τ upon integration and hence not periodic. Therefore we set them equal to zero, obtaining the approximation

$$z = 1 - y J_0(2x) \quad (50)$$

By the y symmetry in equation 45, the y^2 term in the power series in y vanishes. The y^3 term involves a double sum over a product of three Bessel functions, which is inconvenient to evaluate. Bessel functions are always less than one, so equation 50 is a useful approximation for $y \ll 1$. Since Bessel functions fall off as $x^{-1/2}$ for large x and the y^n term is multiplied by n Bessel functions, equation 50 is also useful for $y^2 \ll x$, when x is very large.

We now take up the large problem of a small x approximation

carried to a high order. The equations 44 are three-term recursion relations. In such cases the ratios of coefficients and the z parameter can be expressed in terms of continued fractions. This was the method used by Autler and Townes (1) to solve equations 1. In our notation their equation 11 becomes

$$z = 1 - y + \frac{x^2}{1-y+z-\frac{x^2}{3+y+z-\dots}} + \frac{x^2}{-3-y+z-\frac{x^2}{-5+y+z-\dots}} \quad (51)$$

Autler and Townes evaluated the continued fraction numerically to obtain their plot of the characteristic exponent, but found the evaluation difficult near y equal to an odd integer. We shall use the continued fraction to find z as a power series in x^2 . We could just make a straight algebraic expansion of equation 51, but instead we shall only imagine the expansion, so as to determine the general nature of the coefficients of the various powers of x , and then use undetermined coefficients plus other information to perform the final evaluation.

Let $z = 1 - y - \varphi(x, y)$. Then φ obeys the continued fraction equation

$$\varphi = \frac{x^2}{2(1+y)+\varphi-\frac{x^2}{2(2)+\varphi-\dots}} + \frac{x^2}{2(-1+y)+\varphi-\frac{x^2}{2(-2)+\varphi-\dots}} \quad (52)$$

Let $\varphi(x, y) = \sum \varphi_{2n}(y)x^{2n}$, $\varphi_0 = 0$. From the symmetry relations (equation 45) φ_{2n} is an odd function of y . If we were to compute φ by iterating equation 52 we would find that φ_{2n} are partial fraction functions of y . The denominators $1 \pm y$ would appear in φ_2 . Upon

substituting φ_2 in the right side of equation 52 and expanding, φ_4 would contain $(1 \pm y)^{-3}$. Not until we reach order x^6 in the expansion would $3 \pm y$ appear in the denominator. By thus studying carefully the way in which the expansion of equation 52 would develop one arrives at the following partial fraction expansion for the φ 's:

$$\begin{aligned} \varphi_{2n} = & \sum_{k=1}^{2n-1} \frac{A_k}{(1-y)^k} + \sum_{k=1}^{n-2} \frac{B_k}{(3-y)^k} + \sum_{k=1}^{n-4} \frac{C_k}{(5-y)^k} + \dots \\ & - \sum_{k=1}^{2n-1} \frac{A_k}{(1+y)^k} - \sum_{k=1}^{n-2} \frac{B_k}{(3+y)^k} - \sum_{k=1}^{n-4} \frac{C_k}{(5+y)^k} - \dots \quad (53) \end{aligned}$$

The second line is obtained from the first by antisymmetrization in y . Any sums having an upper limit less than one are to be omitted. This form of φ can also be inferred from the expansion of the infinite determinant performed in Appendix B.

The form given above for z has poles at y equal to odd integers. But we have shown previously that $\cos \pi z/2$ has no poles for finite x and y . The cosine is a function of the square of its argument, so if z^2 has no poles, we are all right:

$$z^2 = (1 - y - \varphi)^2 = (1 - y)^2 - 2(1 - y)\varphi + \varphi^2$$

The cross term and square term permit a possible cancellation of the poles at $y = 1$ in each order in x^2 , so that z^2 can become analytic at $y = 1$. We shall require z^2 to be analytic there. This will give us many relations among the coefficients in equation 53. The cosine is equally well a function of the square of its argument plus any number of

half periods. We shall also require that each of $(z + 2n)^2$ be analytic at $y = 2n + 1$. These requirements are then equivalent to having $\cos \pi z/2$ an entire function of y .

In addition we have from the power series expansion of J_0 in equation 50 that

$$\varphi_{2n} = \frac{(-1)^n}{(n!)^2} y \quad (54)$$

in the limit of small y . From the power series expansion of the elliptic integral in equation 47 we have that

$$\varphi_{2n} = - \left[\frac{(2n-1)!!}{n!} \right]^2 \frac{(-1)^n}{2n-1} y^{-2n+1} \quad (55)$$

in the limit of large y . These relations plus the analyticity requirements are more than sufficient to completely determine the coefficients in equation 53. We shall do the lowest orders to illustrate the method.

For the order x^2 we have from equation 53

$$\varphi_2 = \frac{A_1}{1-y} - \frac{A_1}{1+y}$$

From equation 54: $\varphi_2 = -y$ at small y . Expanding φ_2 the coefficient of y is $2A_1$. Hence $2A_1 = -1$. From equation 55: $\varphi_2 = y^{-1}$ at large y . Expanding φ_2 the coefficient of y^{-1} is $-2A_1$. Hence $-2A_1 = 1$. Both equations give $A_1 = -\frac{1}{2}$. Thus $\varphi_2 = -y(1 - y^2)^{-1}$.

For the order x^4 we have from equation 53

$$\varphi_4 = \frac{A_1}{1-y} - \frac{A_1}{1+y} + \frac{A_2}{(1-y)^2} - \frac{A_2}{(1+y)^2} + \frac{A_3}{(1-y)^3} - \frac{A_3}{(1+y)^3}$$

From equation 54: $\varphi_4 = \frac{1}{4} y$ at small y , giving us the relation $2A_1 + 4A_2 + A_3 = \frac{1}{4}$. From equation 55: $\varphi_4 = -(\frac{3}{4}) y^{-3}$ at large y ,

giving us two equations, since there must be no term in y^{-1} :

$$-2A_1 = 0 \qquad -2A_1 + 4A_2 - 2A_3 = -\frac{3}{4}$$

For analyticity about $y = 1$ we expand z^2 in powers of x and make coefficients of each power analytic:

$$z^2 = (1 - y - \varphi)^2 = (1-y)^2 - 2(1-y)\varphi_2 x^2 - 2(1-y)\varphi_4 x^4 + \varphi_2^2 x^4 + O x^6$$

From its form in equation 53, $(1-y)\varphi_2$ has no pole at $y = 1$. In order to make $-2(1-y)\varphi_4 + \varphi_2^2$ analytic at $y = 1$ we expand φ_2^2 in a partial fraction series. We have terms in $(1-y)^{-1}$ and $(1-y)^{-2}$ from both φ_2^2 and $(1-y)\varphi_4$. By requiring these to cancel we obtain the relations

$$-2A_2 - \frac{1}{4} = 0 \qquad -2A_3 + \frac{1}{4} = 0$$

Altogether we have five equations for the three coefficients. They have the consistent solution

$$A_1 = 0 \qquad A_2 = -\frac{1}{8} \qquad A_3 = \frac{1}{8}$$

For the order x^6 we have six coefficients to find, including five A 's and B_1 . To remove the new pole at $y = 3$ we require $(z + 2)^2$ to be analytic there or $(3-y)\varphi_6$ analytic at $y = 3$, which it is by equation 53. At $y = 1$ we require analyticity of $-2(1-y)\varphi_6 + 2\varphi_2\varphi_4$, giving us four immediately soluble relations. From the large y approximation we get three, and from the small y approximation, one more equation. The eight equations for six unknowns have consistent solutions, of course. The extra equations provide a check on the arithmetic.

Although this procedure is awkward to describe, it requires enough less algebra than more direct methods of obtaining the expansion in x , that it has been successfully carried through order x^8 . Half of the work in this high order was the reduction from the partial fraction series to a more compact form. The final result is

$$\begin{aligned}
 z = 1 - y + \frac{y}{1-y^2} x^2 - \frac{y(1+3y^2)}{4(1-y^2)^3} x^4 + \frac{y^3(1+y^2)}{(1-y^2)^5} x^6 \\
 + \frac{y}{4(1-y^2)^2(9-y^2)} x^6 - \frac{3}{8} \frac{y^3}{(1-y^2)^5} x^8 - \frac{5}{4} \frac{y^5(3+y^2)}{(1-y^2)^7} x^8 \\
 - \frac{5}{4} \frac{y^3(5-y^2)}{(1-y^2)^4(9-y^2)^2} x^8 - \frac{9}{64} \frac{y}{(1-y^2)^2(9-y^2)^2} x^8 \\
 + \text{order } x^{10}
 \end{aligned} \tag{56}$$

For computation we would not always use this equation itself, but $(z+2n)^2$, since these series converge faster. For y between 0 and 2 we would use

$$\begin{aligned}
 z^2 = (1-y)^2 + \frac{2y}{1+y} x^2 - \frac{y}{2(1+y)^3} x^4 + \frac{y(1-5y-2y^2)}{2(1+y)^5(9-y^2)} x^6 \\
 + \text{order } x^8
 \end{aligned} \tag{57}$$

and for y between 2 and 4

$$\begin{aligned}
 (z+2)^2 = \left[3 - y + \frac{y}{1-y^2} x^2 - \frac{y(1+3y^2)}{4(1-y^2)^3} x^4 + \frac{y^3(1+y^2)}{(1-y^2)^5} x^6 \right]^2 \\
 + \frac{y}{2(1-y^2)^2(3+y)} x^6 + \text{order } x^8
 \end{aligned} \tag{58}$$

and so on for other regions in y . However equation 56 is satisfactory for regions between narrow resonances. These series are good enough approximations to reproduce the numerical results of Autler and Townes.

The locations of the various resonance peaks are found by solving $\partial(z+2p)/\partial y = 0$ for y . Using an iterative solution we find these peak locations as power series in x . The x^2 term will just give us the same results as perturbation theory (compare equation 37). However higher order terms are not too difficult to evaluate from equations 56 to 58. For the primary resonance we obtain from equation 57 the peak location:

$$y = 1 - \frac{x^2}{4} - \frac{5x^4}{64} - \frac{61x^6}{2048} - \dots$$

Converting to dimensional notation and solving for ω instead of ω_0 the resonance condition is

$$\omega = \omega_0 + \frac{c^2}{\omega_0} + \frac{c^4}{4\omega_0^3} - \frac{35c^6}{32\omega_0^5} - \dots \quad (59)$$

The c^2 term is the Bloch-Siegert shift and the next two terms are the higher order corrections to it. One would have to go to sixth order to obtain this result by perturbation theory.

With all the preceding approximations there is still a sizeable gap between small and large y at large x in which we know nothing about the behavior of z . There seems little hope of finding any known function which looks like Bessel functions at small y and elliptic integrals at large y . Hence resort was finally made to numerical computations. The method used was to integrate the differential equation numerically over one period and thus obtain the A matrix of chapter VI. The

characteristic exponents are found from the eigenvalues of A . The last step is particularly easy for a two level problem with traceless Hamiltonian. For then the matrix of characteristic exponents Q is of the form $q\sigma_z$. Hence $\text{Tr } e^{-iQT} = \text{Tr } A = 2 \cos qT$. If the α and β in equation 41 are fixed by the initial conditions $\alpha(0) = 1$, $\beta(0) = 0$, then

$$A = U(T;0) = \begin{pmatrix} \alpha(T) & -\beta^*(T) \\ \beta(T) & \alpha^*(T) \end{pmatrix}$$

where T is the period and the second column was determined by the restriction that A be unitary and have determinant one. Taking the trace of A we find $\cos qT = \text{Re } \alpha(T)$, or in our dimensionless notation

$$\cos \frac{\pi z}{2} = \text{Re } \alpha \left(\frac{\pi}{2} \right) \quad (60)$$

A program was written for the Burroughs 220 electronic digital computer at the Institute, taking advantage of an existing subroutine for numerical integration of differential equations by the Runge-Kutta method. The program actually integrated equations 49 with $a(0) = 1$, $b(0) = 0$ up to $\tau = \pi/2$. It then computed z by the formula

$$z = \left(\frac{2}{\pi} \right) \cos^{-1} \left[-\text{Im } \alpha \left(\frac{\pi}{2} \right) \right] \quad (61)$$

which is equivalent to equation 60. The inverse cosine subroutine automatically selected that branch of z lying between 0 and 2. The normalization $|a(\tau)|^2 + |b(\tau)|^2$ was also printed out. Its deviation from unity gives a rough measure of the accuracy of the integration. As x and y increase the right-hand side of equation 49 varies more rapidly and one

has to use a smaller interval in the numerical integration to retain accuracy. Hence even with a computer it takes more time to get results for large x .

The data from the computer was first used to verify the various analytical approximations. In particular it was found that equation 57 gives the value of z to within 0.002 for $x = 1$ and y anywhere between 0 and 2, being even an order of magnitude better at $y = 1$ and near $y = 0$. Equation 58 gives comparable results for y between 2 and 4, while equation 56 is satisfactory for larger values of y . These equations still give some good results at $x = 1-1/2$, but have rather large errors for $x = 2$, since terms in x^{10} are then important. The agreement between the results of machine computation and analytical approximations was particularly encouraging because of the disparity in the methods.

The computer was then used to map out the characteristic exponent z in the region $y = 0$ to 5 and $x = 0$ to 6. From a study of this data it was easy to infer the behavior of z for all x and y . Sample curves of z as a function of y in the range 0 to $7-1/2$ are shown for $x = \frac{1}{2}$, 1, and 3 in figures 6a - 8a. We shall discuss the meaning of figure 6a in detail and then indicate how increasing x modifies the picture.

For the "small" value $x = 1/2$ (this corresponds to $H_1 = H_0$ for a spin $1/2$ particle in magnetic fields) we see from figure 6a that z is essentially a triangular wave as in the limit of small x , except around $y = 1$ where the corner is nicely rounded off. Actually all the corners

are rounded, but as y increases this rounding occurs on too small a scale to show in the figure. In figure 5 we show this same curve together with several other branches of z . Wherever we have a corner in one branch we have one in the other branches such that two branches come very close to each other. By the arguments of chapter V we then say that the corners of the triangular wave in any branch of z are actually little hyperbolae and correspond to resonances in the probability for transition from state α to β . The corners near $y = 3, 5, 7$, etc., correspond to three, five, seven and more quantum resonances of the type discussed in chapter VII. From equation 16 the distance by which a rounded corner falls short of the bounding line $z = 0$ or 2 , which is half the distance to the other branch of the little hyperbola, corresponds to half the width of the resonance. These widths were determined by perturbation theory in chapter VII (equation 37) and found to be exceedingly small for the higher resonances. For the resonances near $y = 3, 5$, and 7 in figure 6 these widths are 1.6×10^{-2} , 6×10^{-5} and 10^{-7} respectively. Since the separation of the resonances is large compared to the widths in the triangular wave region of the z curve, the Rabi-type formula (equation 7) gives a good representation of the resonance line shape.

The broadly rounded corner near $y = 1$ corresponds to a broad resonance. For such broad resonances, and inbetween resonances, i. e. anywhere that z is not close to any of its other branches, the $2z$ frequency of oscillation in a Rabi-type formula becomes comparable with the frequency of the oscillating field, which is usually rapid compared to the action of any relaxation mechanism or the response of physical apparatus detecting the occurrence of transitions. What one observes in

these cases is the all time average transition probability of equation 30. For our two-state system we can use the special result equation 43 to obtain the average transition probability directly from a graph of z as a function of y . Equation 43 is what we have plotted below the corresponding z curve in figures 6b - 9b. By comparing the lower or transition probability curves with the upper or characteristic exponent curves one can learn to visualize the lower curve when only the upper one is available. Thus the resonances in the lower curve, figure 6b, corroborate our description of the resonances implied by the upper curve, figure 6a.

The vertical lines represent resonances whose widths are too narrow to show on the scale chosen, although they all reach the theoretical maximum height of one half. In a physical experiment the finite resolving power of the apparatus reduces the height of narrow resonances, so much so that those of very tiny widths are not observed at all. For example, if in observing the line shape shown in figure 6b we had a resolving power of 10^{-3} (e. g. in magnetic resonance our static magnetic field H_0 were constant to one part in a thousand), then the $y \approx 3$ resonance would have the full height shown, the $y \approx 5$ resonance would have one sixteenth that height and the $y \approx 7$ resonance would not be seen. In normal spectroscopic work x is very small and only the primary resonance is wide enough to be seen. This is quite fortunate, for spectra are complicated enough as it is without having to worry about a series of multiple quantum transitions for each line.

As we increase x each resonance broadens and shifts toward

smaller values of y . This is clearly shown in figure 7 where $x = 1$ ($H_1 = 2H_0$). The fundamental single quantum resonance has moved to $y = 0.7$ or $\omega = 1.4 \omega_0$. It has also become so broad that the triple quantum resonance sits on the side of it and the higher resonances sit on its tail. The large transition probability at $y = 0$ arises from the overlap of the single quantum resonance transition with its "image" at negative y . (The antisymmetry of z implies symmetry of the time average transition probability in y .) The curves for $x = 1/2$ and $x = 1$ (figures 6 and 7) can be obtained from equations 56, 57, and 58 together with 43, plus perturbation theory for the widths of higher order resonances.

As we increase x further the slope of z at $y = 0$ changes from negative to positive. As this happens the peak of the primary resonance moves to $y = 0$, meets its image there, and then disappears, leaving a very high and broad "background" transition probability centered at $y = 0$. The next or three-quantum resonance moves toward $y = 0$ and broadens until eventually it too reaches its image at $y = 0$ and disappears. Before it so disappears theoretically, as indicated by the vanishing of a peak reaching to one half, it may disappear experimentally because its amplitude over that of the background becomes very small.

In figure 8 we show the strong field case $x = 3$ ($H_1 = 6H_0$). Here the single and triple quantum resonances have both disappeared and the five-quantum resonance is on its way. The latter has shifted all the way from $y = 5$ to $y = 2.85$ and acquired a width of about 0.5. This width still agrees surprisingly well with the perturbation theory prediction for

the width: $x^5/512 = 0.47$. The next resonance is still much narrower with a width of 0.04. The background transition probability now extends to large values of y .

As we increase x still further this same general behavior continues. The z curves become flatter for y the order of one, then after only one or two broad swings they approach triangular waves. The period of the triangular wave decreases as y increases, until it eventually comes close to the large y (and small x) limit of 4 with the corners approaching their positions for $x = 0$. The transition region between $z(y)$ linear at small y and triangular wave at large y is never very large and nothing unusual occurs there. The time average transition probability shows with rising x an ever widening background with one or two side peaks of appreciable width, but shifted very far from their "home" positions at $x = 0$. Numerical calculations on the computer were necessary to obtain figure 8 for $x = 3$ and have been done at $x = 8$, confirming the general behavior we have outlined.

In addition to detailed plots like those in figures 6 - 8 we can obtain some information on transition probabilities by applying equation 43 to our analytical approximations. From the large y approximation equation 48 we obtain

$$\overline{P} = \frac{x^2}{y^2} - \frac{11x^4}{4y^4} + \dots$$

This gives the magnitude of the background transition probability for large x and very large y . For modest values of x and any y not close to 1 a better approximation for the background comes from the x^2

term of equation 56:

$$\overline{P} = \frac{1 + y^2}{(1 - y^2)^2} x^2 + \text{order } x^4$$

These two approximations are good when they give a small \overline{P} . From the small y approximation, equation 50, we obtain

$$\overline{P} \approx \frac{1}{2} [1 - J_0^2(2x)]$$

For small x we have $\overline{P} \approx x^2$ in agreement with the preceding equation for $y = 0$. As x increases J_0 has roots which make \overline{P} go to its maximum of $1/2$. These roots tell us at just what value of x the various resonances are shifted into the origin to disappear. Thus at any given x we can tell how many resonances we have lost.

On figures 6b - 9b we have plotted the transition probability as a function of the unperturbed level separation ω_0 , keeping the ratio c/ω fixed. Frequently one records resonances by varying ω and keeping c and ω_0 constant. In such a plot the primary resonance will broaden and shift outward to larger ω as c/ω_0 increases. The other resonances will follow after from their jammed up position near $\omega = 0$, riding the back slope of the primary resonance (figure 10). In this way of plotting, our small y approximation holds in all the region of $\omega \gg \omega_0$ giving us $\overline{P} = \frac{1}{2} [1 - J_0^2(\frac{4c}{\omega})]$. This function of ω has broad resonances with peaks at $\omega = 4c/r_n$, where the r_n are the roots of J_0 . If c/ω is large enough, some of these peaks will occur within the region of validity of this approximation and give us the actual positions of resonances, where these positions are now large compared to the original resonance frequency. Thus the asymptotic position of the primary resonance (equation

59 in the limit $c \gg \omega_0$) is $1.663c$.

Because of the increasing background or nonresonant transition probability, the time average transition probability at any fixed value of ω and ω_0 increases toward the limiting value of $1/2$ as c increases. When c becomes large compared to ω_0 , the oscillating field is much stronger than the static or atomic field producing the energy separation ω_0 . Hence a particle, such as an electron in the magnetic field of a nucleus, is more strongly coupled to the oscillating field than to the nuclear field. It then tries to follow the oscillating field and its state, defined relative to the nuclear field, becomes unimportant in its motion. Its motion might then make it appear as if on the average it spent half its time in each state.

Before anyone rushes out to experimentally test these results we should give some idea of just how strong an oscillating field is required. Suppose we wish to make $x = 1$. Then for our radio frequency example in chapter IV we would need a peak field strength of about 16 gauss or 5 kilovolts/cm. This kind of field strength is readily attainable. However, for our microwave example in chapter VII we would need a field strength of about 10^6 volts/cm or the order of 10^9 watts power input to the resonant cavity. This would be near or beyond the limit of present technology. At the frequency of the ruby laser a field strength of the order of 10^8 volts/cm would be required. This is about 15 times greater than a theoretical maximum attainable field within the ruby and at least

100 times greater than any fields actually produced.

Oscillating fields of such great strengths can cause other phenomena as well as rapid transitions between levels. Fontana, Pantell and Smith (38) found that a microwave field with a peak field strength greater than 25 kilovolts/cm caused ammonia molecules to ionize and form a plasma, whose behavior requires a completely different theory. Thus in some experimental situations it may not even be possible to apply such strong fields without producing conditions for which the theory does not apply.

IX. EXTENSIONS TO MORE COMPLEX CASES

We shall now discuss some of the phenomena and difficulties encountered in trying to extend the methods of chapters VII and VIII to more complex problems. We shall first deal with the two state system under a general type of oscillating interaction. Then we shall discuss a problem with three atomic states, and finally we shall mention the effects of additional frequencies of excitation. The general outcome is that the perturbation method is as effective with more complex cases as it was in chapter VII, while the methods of chapter VIII are not. Some guidelines are given to help minimize the amount of numerical computation necessary if a complex problem must be solved in detail.

In order to understand the possible generalizations of the form of an oscillatory interaction in a two-state system we shall use the language which particularly describes the magnetic resonance problem. As noted by Bloch and Siegert (30) one can excite a magnetic transition with an elliptically polarized field, as well as a linearly or circularly polarized one. That is we can have rotating and antirotating components of the field with different magnitudes. This is described mathematically by replacing $2c \cos \omega t$ in equation 1 with $ce^{i\omega t} + c'e^{-i\omega t}$, where c and c' can now be unequal. By appropriate choice of the zero for time and the relative phases of the amplitudes we can still have c and c' real. It is also possible to have a component of the oscillating field parallel to the z axis. This has the effect of modulating the energy separation ω_0 . Since it could have any phase relative to the perpendicular field, we describe it mathematically by adding $2g \cos (\omega t - \delta)$ to E_a and

- $2g \cos (\omega t - \delta)$ to E_β . Note that adding oscillating terms of the same sign and magnitude to E_α and E_β will have no effect on transition probabilities, for they can be removed by a phase factoring transformation with an oscillatory phase. Since the same phase would be used for both states, these phase factors will cancel out in the density matrix. The A^2 term that comes with a $\vec{p} \cdot \vec{A}$ interaction is of this form and thus does not contribute to transition probabilities.

The generalized traceless Hamiltonian for the time-dependent two-state Schrödinger equation is

$$\mathcal{H}_C = \begin{pmatrix} \frac{\omega_0}{2} + 2g \cos (\omega t - \delta) & ce^{-i\omega t} + c'e^{i\omega t} \\ ce^{i\omega t} + c'e^{-i\omega t} & -\frac{\omega_0}{2} - 2g \cos (\omega t - \delta) \end{pmatrix} \quad (62)$$

It can describe any orientation of elliptically polarized radiation exciting the system. The most common case experimentally would be an inclined oscillating field for which $c = c'$, $\delta = 0$.

Our first step in the solution of equation 1 was to perform a phase factoring to make part of the off diagonal elements time independent, and the rest have frequency 2ω . This phase factoring is less useful now, since it does not affect the g terms. The resulting \mathcal{H}_C would still have terms with frequency ω as well as 2ω . So we shall take equation 62 as it is and write the Floquet Hamiltonian corresponding to it from equation 23:

$$\begin{pmatrix}
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
 \cdot & -\omega + \frac{1}{2}\omega_0 & 0 & g & c & 0 & 0 & 0 & 0 & 0 & \cdot & \alpha -1 \\
 \cdot & 0 & -\omega - \frac{1}{2}\omega_0 & c' & -g & 0 & 0 & 0 & 0 & 0 & \cdot & \beta -1 \\
 \cdot & g^* & c' & \frac{1}{2}\omega_0 & 0 & g & c & 0 & 0 & 0 & \cdot & \alpha 0 \\
 \cdot & c & -g^* & 0 & -\frac{1}{2}\omega_0 & c' & -g & 0 & 0 & 0 & \cdot & \beta 0 \\
 \cdot & 0 & 0 & g^* & c' & \omega + \frac{1}{2}\omega_0 & 0 & g & c & 0 & \cdot & \alpha 1 \\
 \cdot & 0 & 0 & c & -g^* & 0 & \omega - \frac{1}{2}\omega_0 & c' & -g & 0 & \cdot & \beta 1 \\
 \cdot & 0 & 0 & 0 & 0 & g^* & c' & 2\omega + \frac{1}{2}\omega_0 & 0 & 0 & \cdot & \alpha 2 \\
 \cdot & 0 & 0 & 0 & 0 & c & -g^* & 0 & 2\omega - \frac{1}{2}\omega_0 & 0 & \cdot & \beta 2 \\
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
 \end{pmatrix} \quad (63)$$

The phase difference δ has been put into g as a complex phase angle. The quantum numbers of the Floquet states have been listed on the right. The field quantum numbers are $2p$ or $2p + 1$ compared to the corresponding numbers p in equation 32 because we have not done the phase factoring.

In the weak field case, $c, c', g \ll \omega$ we can look for cases where a pair of Floquet states in equation 63 are nearly degenerate and then apply perturbation theory to get transition probabilities of the form of equation 7, just as we did in chapter VII for the case $c' = 0, g = 0$. We find that $|\alpha 0\rangle$ is degenerate with $|\beta n\rangle$ when $n\omega = \omega_0$. Because the g 's couple all states with the same atomic quantum number but different field quantum numbers to each other, we can always find matrix elements connecting $|\alpha 0\rangle$ to $|\beta n\rangle$ for all integers n . Hence multiple quantum jumps involving one, two, three, ... photons are all possible. From the

point of view of angular momentum selection rules for magnetic resonance the oscillating field in the z direction carries no angular momentum in the z direction. Thus by taking $n - 1$ of such photons with $M_z = 0$ and one rotating photon ($M_z = +1$) we can make the transition from $m = -\frac{1}{2}$ to $m = +\frac{1}{2}$ with n quanta. These transitions have been predicted previously by Winter (2) and shown experimentally by Margerie and Brossel (4). As in the simpler case the resonance shifts, but only the order of magnitude of the widths, were given by Winter (21). We can find both by the methods already developed. We shall do a few cases to illustrate the kind of results one encounters.

Let us first consider a double quantum transition from $|\alpha 0\rangle$ to $|\beta 2\rangle$. We assume these states are nearly degenerate in equation 63:

$$\frac{1}{2} \omega_0 \approx 2\omega - \frac{1}{2} \omega_0 \approx q \quad \text{or} \quad 2\omega \approx \omega_0 \approx 2q$$

and apply the perturbation theory of Appendix A. The V_{pp} sum of equation A7 now has several non-zero terms:

$$\frac{c^2}{q - \omega + \frac{1}{2} \omega_0} + \frac{c'^2}{q + \omega + \frac{1}{2} \omega_0} + \frac{|g|^2}{q - \omega - \frac{1}{2} \omega_0} + \frac{|g|^2}{q + \omega - \frac{1}{2} \omega_0}$$

We approximate the denominators by replacing q and ω_0 by ω and 2ω respectively, obtaining $\frac{c^2}{\omega} + \frac{c'^2}{3\omega}$. The cancellation of the lowest order shifts produced by the g 's occurs for all states, so that none of our transitions has a $|g|^2$ shift. The g does contribute to frequency shifts in higher orders, however. The V_{pq} interaction contains two terms of second order

$$\frac{-cg}{q - \omega + \frac{1}{2}\omega_0} + \frac{gc}{q - \omega - \frac{1}{2}\omega_0}$$

which become equal upon approximating the denominators. These two terms correspond to the two different orders in which the two polarizations of photons ($M_z = 1, 0$) can be absorbed or emitted. Our two by two approximate matrix becomes

$$\begin{pmatrix} \frac{1}{2}\omega_0 + \frac{c^2}{\omega} + \frac{c'^2}{3\omega} & -\frac{2cg}{\omega} \\ -\frac{2cg}{\omega} & 2\omega - \frac{1}{2}\omega_0 - \frac{c^2}{\omega} - \frac{c'^2}{3\omega} \end{pmatrix}$$

From this we read off the parameters for the transition probability relation equation 7, finding $n = 2$, $\omega_{res} = \omega_0 + \frac{2c^2}{\omega} + \frac{2c'^2}{3\omega}$ and $u = -\frac{4cg}{\omega}$.

As a numerical example consider again an atomic beam experiment with a transition frequency of 10^{10} cps and a line width of 10^4 cps. Consider the case $c = c' = g$. Then if one milliwatt input power excites the single quantum transition optimally, 450 watts are required to excite the double quantum transition optimally and the resonance frequency is shifted 2 kc from $\frac{1}{2} \times 10^{10}$ cps, or the order of one line width. This is not as bad a situation as the three quantum transition described in chapter VII, but is much worse than the two quantum transition described in chapter IV. The reason is the much larger degree of energy non-conservation in the intermediate state for the present case. The "half frequency" transitions at about 3 MC observed by Hughes and Grabner in the rotational spectra of RbF (26) were presumably of this type, but with more than two states involved.

The three-quantum transition with a g term present can take place by several paths. In addition to the absorption of photons with $M_z = +1, -1, +1$ described in chapter VII, we have the possibility for absorption of photons with $M_z = +1, 0, 0; 0, +1, 0$; and $0, 0, +1$, all of which represent distinct terms in the interaction matrix element γ_{pq} . These various terms can interfere with each other. Working out the perturbation theory we find the parameters for equation 7 to be $n = 3$,

$$\omega_{\text{res}} = \omega_0 + \frac{c^2}{\omega} + \frac{c'^2}{2\omega}, \quad u = -\frac{c^2 c'}{2\omega^2} + \frac{4cg^2}{\omega^2} \quad \text{or:}$$

$$|u|^2 = \frac{\frac{1}{4} c^4 c'^2 - 4c^3 c' |g|^2 \cos 2\delta + 16c^2 |g|^4}{\omega^4}$$

By varying the value of g relative to c one varies the width considerably. In the special situation $c = c' = \sqrt{8} g = \sqrt{8} g^*$ the above width vanishes. However there may still be a higher order term in u which does not vanish.

Transitions with $n = -1, -2, -3$, etc. are the same as those for positive n except that c and c' interchange roles and the phase difference δ reverses sign. Not to slight any of the integers we should also include $n = 0$. Our perturbation theory gives us a resonance between $|a0\rangle$ and $|\beta0\rangle$ in second order with $n = 0$, $\omega_{\text{res}} = \omega_0 + \frac{2(c'^2 - c^2)}{\omega}$ and $u = 4(cg^* - c'g)/\omega$. This resonance corresponds to the absorption of an $M_z = +1$ photon followed by the emission of an $M_z = 0$ photon, or the absorption of an $M_z = 0$ photon followed by the emission of an $M_z = -1$ photon. Since $n = 0$ the resonance is located at $\omega_{\text{res}} = 0$ or $\omega_0 = 2(c^2 - c'^2)/\omega$ or $\omega = 2(c^2 - c'^2)/\omega_0$ where $\omega \gg c \gg \omega_0$. Because

of the latter inequality we have in a sense a strong field situation.

For the two state system with a generalized oscillatory interaction the special formula equation 39 still applies for the time average transition probability and resonances are located at $\partial q / \partial \omega_0 = 0$ where q is the characteristic exponent. The determination of q is much more difficult than it was in chapter VIII, because of the increased number of parameters and more involved couplings of states. We shall not try to do much more than we already have with perturbation theory. However we indicate briefly which of the methods of chapter VIII are still applicable. The dimensionless notation can still be used with the additional definitions $x' = 2c'/\omega$, $w = 2g/\omega$. The characteristic exponent z now has frequency 2 (period π) instead of 4. In the limit of small oscillating perturbation z is approximately the triangular wave extension of $1 - y$ running in strips of height one. There are few symmetries in the general case. However in the special case $x' = x$, w real, z is symmetric about $y = 0$; while for $x' = 0$, z is symmetric about $y = 1$. The z values are normally not degenerate, but "accidental" degeneracy is possible. For example it occurs at $x = x'$, w real, $y = 0$ where $z = 1 = 2 - z$. The large y approximation can be carried through as in chapter VIII except that the integral cannot be expressed in terms of a simple tabulated function. However we can obtain a series expansion of the integral analogous to equation 48. The small y approximation method of chapter VIII fails completely except when $x = x'$, w real. In this oscillating field case we can, by choosing a linear combination of a and b which diagonalizes the part of \mathcal{H}_C proportional to $\cos 2\tau$, obtain

$$z \approx 1 - (y/v) [w^2 + x^2 J_0^2(2v)]^{1/2}$$

where $v^2 = w^2 + x^2$. No real attempt has been made to find a partial fraction series analogous to equation 53.

The computer method for finding z does work with equations 62 and the program was generalized to handle them. Because of the longer period we must integrate the differential equation twice as far as before to obtain z . This doubling of the integration time along with the larger number of parameters discouraged an extensive study of z with the computer. A few trial runs showed the same type of behavior as for the simpler case except, as already noted, resonances occur twice as often. In figure 9 we show sample curves of z and the time average transition probability for the parameters $x = x' = w = w^* = 0.6$. By imagining an experimental resolving power to reduce the height of the narrow four quantum peak and some sort of experimental damping of the amplitude at small y , figure 9b is in qualitative agreement with the experimental strong field curve of Margerie and Brossel (4, figure 2). Due to lack of experimental details a quantitative comparison is not possible.

We shall now discuss the problem of three atomic states connected by an oscillating perturbation. We treated this problem in chapter IV using the rotating field approximation, but we now retain all of the oscillatory perturbation. The energy level scheme and parameters are shown in figure 2. After phase factoring \mathcal{H}_C has frequency 2ω and is given in equation 8. The Floquet Hamiltonian corresponding to this \mathcal{H}_C is

$$\begin{pmatrix}
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
 \cdot & -2\omega - \Delta - \frac{a}{3} & 0 & b & 0 & 0 & 0 & 0 & \cdot \\
 \cdot & 0 & \left[\begin{array}{ccc} \Delta - \frac{a}{3} & c & 0 \end{array} \right] & 0 & 0 & 0 & 0 & \cdot \\
 \cdot & b & \left[\begin{array}{ccc} c & \frac{2a}{3} & b \end{array} \right] & c & 0 & \cdot & \cdot & \cdot \\
 \cdot & 0 & \left[\begin{array}{ccc} 0 & b & -\Delta - \frac{a}{3} \end{array} \right] & 0 & b & \cdot & \cdot & \cdot \\
 \cdot & 0 & 0 & c & 0 & 2\omega + \Delta - \frac{a}{3} & c & \cdot \\
 \cdot & 0 & 0 & 0 & b & c & 2\omega + \frac{2a}{3} & \cdot \\
 \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
 \end{pmatrix}
 \begin{matrix}
 \cdot & \cdot \\
 \gamma & -1 \\
 a & 0 \\
 \beta & 0 \\
 \gamma & 0 \\
 a & 1 \\
 \beta & 1 \\
 \cdot & \cdot
 \end{matrix}
 \quad (64)$$

where the Floquet state quantum numbers are indicated on the right.

In chapter IV we considered only the three by three block of \mathcal{H}_F outlined by dashed lines. With the full Floquet Hamiltonian we can map out the complete spectrum of multiple quantum transitions by finding for which frequencies two diagonal elements become degenerate. For transitions from atomic state a to atomic state β we set the unperturbed energies of $|a0\rangle$ and $|\beta n\rangle$ equal, obtaining

$$2n\omega = \Delta - a \quad \text{or} \quad (2n+1)\omega = E_a - E_\beta$$

Hence we expect multiple quantum transitions to occur whenever the energy separation $E_a - E_\beta$ equals an odd harmonic of the driving frequency, just the same rule we found in chapter VII for the case of two atomic states. For transitions between atomic states β and γ we have a similar result. Resonances occur when

$$2n\omega = \Delta + a \quad \text{or} \quad (2n+1)\omega = E_\beta - E_\gamma$$

These two cases in the three level system have the same selection rule

as for the two level problem, but not the same answer, since the third level contributes to the shifts and widths of the transitions by acting as an alternative intermediate state.

For transitions between atomic states α and β we find resonances when

$$2n\omega = 2\Delta \quad \text{or} \quad (2n + 2)\omega = E_{\alpha} - E_{\gamma}$$

Hence we expect multiple quantum transitions to occur whenever the energy separation $E_{\alpha} - E_{\gamma}$ equals an even harmonic of the driving frequency. The two-quantum transition was discussed in chapter IV. As a representative example of the results one can get in complex multiple quantum transitions we give here the parameters in equation 7 which make it describe the four-quantum transition between states α and γ . We find by perturbation theory $n = 4$, $\omega_{\text{res}} = E_{\alpha} - E_{\gamma} + \frac{c^2}{\omega - a} + \frac{c^2}{3\omega - a} + \frac{b^2}{\omega + a} + \frac{b^2}{3\omega + a}$ and $u = bc(c^2 - b^2)/\omega(\omega^2 - a^2)$. Note that this transition is enhanced (u increased) when $a \approx \pm \omega$, since the intermediate level β is then in such a position that energy is nearly conserved in one of the four emissions or absorptions. However it will still require stronger fields to observe than were required for the three quantum transition described in chapter VII. In the radio frequency example of chapter IV an H_1 of about 5 gauss would be required to observe this transition. A factor of three in this estimate is due to the fact that b and c are nearly equal, making u considerably smaller than an order of magnitude estimate.

The methods of chapter VIII are of little avail on the three state problem. We no longer have a simple relation like equation 39 to give

us transition probabilities directly from the characteristic exponents, but must fall back on the general formulae of chapter VI. Numerical integration of the differential equation can give the characteristic exponents through the A matrix, but the integration would have to be done twice with different initial conditions before A could be determined. Computation of transition probabilities by integrating the differential equation is tedious because a large number of integrations must be done in order to average over initial or elapsed times. The best method would probably be to diagonalize the Floquet Hamiltonian directly with a fast computer. One should first look only at the eigenvalues as a function of a y parameter in order to locate resonances as described in chapter V. Then one can compute eigenvectors at the points of interest. The periodicity properties of the Floquet Hamiltonian make it unnecessary to compute more than three eigenvalues and eigenvectors. Truncation of the Floquet Hamiltonian causes no serious error. To get eigenvalues within an absolute error ϵ one need take a block of \mathcal{N}_F just large enough so that all components greater than ϵ are obtained for the eigenvectors corresponding to eigenvalues in the middle of the block.

If we excite our system with two or more commensurable frequencies we can still use the general theory of chapter VI, but \mathcal{N}_F will have a much more complex structure than the one in equation 22. With only a single frequency of excitation the system absorbs and emits photons at this one frequency. But with harmonic frequencies present in the excitation the system could absorb photons at one frequency and emit at another. This complicates the picture considerably, but also makes it

more interesting, because of the possibility of finding conditions with respect to the natural atomic frequencies at which an atom might translate power from one frequency to another, i. e. act as a frequency multiplier or divider. However the theory of chapter VI treats atomic transition probabilities, not radiation field transition probabilities. It is not suitable for treating absorption and induced emission at harmonic frequencies, since the Floquet states do not distinguish between two photons of frequency ω and one photon of frequency 2ω .

Finally we mention what happens if we excite our system with two incommensurable frequencies ω and ω' . In the first place our Hamiltonian will not be periodic so all the theory of chapter VI is useless. However if $\omega - \omega'$ is small compared to either ω or ω' we have an approximation possibility. Suppose our interaction matrix element in \mathcal{H}_C is $2c \cos \omega t + 2b \cos \omega' t$. If we write this in exponential form and perform a phase factoring to make one exponential term constant, we get

$$c + ce^{2i\omega t} + be^{i(\omega+\omega')t} + be^{i(\omega-\omega')t} \quad (65)$$

If we now neglect the two middle terms as being more rapidly oscillating, we have only the single frequency $\omega - \omega'$ in the Hamiltonian and can apply the theory of chapter VI. We can use this approximation, for example, to find that the presence of ω' produces a shift in the ω resonance of approximately $2b^2/(\omega - \omega')$. Note the similarity of this shift to that computed in chapter IV for the case of an additional state: $b^2/(\omega_0 - \omega_1)$, where ω_0 and ω_1 are natural frequencies (energy level separations) of the atomic system rather than frequencies of the radiation field.

In general each exponential term in equation 65 produces a shift. In lowest order these shifts add, giving a total shift

$$\frac{2c^2}{\omega - (-\omega)} + \frac{2b^2}{\omega - (-\omega')} + \frac{2b^2}{\omega - \omega'} = \frac{c^2}{\omega} + \frac{4\omega b^2}{\omega^2 - \omega'^2} \quad (66)$$

As we have written it the Bloch-Siegert shift (first term) is seen to be a shift due to the presence of another excitation frequency $-\omega$, and is of exactly the same form as the other terms. Thus a resonance transition is produced by one exponential component of an exciting field, while the other component and any other exciting fields produce in first approximation only small frequency shifts.

If the oscillating field at frequency ω' connects atomic state pairs different from those connected by ω , it is often possible to perform a phase factoring and obtain a rotating field approximation containing part of both interactions. For example in the three level \mathcal{H}_C of chapter IV we could replace $b \cos \omega t$ by $b \cos \omega' t$. By a slightly different choice of μ , ν and ξ we would obtain after phase factoring the same time independent part of \mathcal{H}_C' as in equation 8. Such an approximation was used by Javan in his treatment of the three level maser (17).

X. QUANTIZED FIELD TREATMENT

In this chapter we shall consider the radiation field to be a quantum system, as well as the atom. Then by taking the limit of large quantum numbers for the field, we shall see how this theory goes over into the theory given in chapter VI. Finally we discuss some of the improved physical interpretations provided by a quantized field viewpoint.

We write the total Hamiltonian as a sum of three parts representing the atomic system, the radiation field, and their interaction respectively:

$$\mathcal{H}_Q = \mathcal{H}_a + \mathcal{H}_f + \mathcal{H}_i$$

The radiation field, when quantized in a cavity, is in general made up of an infinite number of uncoupled harmonic oscillators with frequencies determined by the dimensions of the cavity. In the preceding work we considered primarily a single frequency of excitation, hence we shall here consider only a single mode of the field to be excited. Then we can use \mathcal{H}_f as just the Hamiltonian for a single quantum-mechanical oscillator of frequency ω .

We shall work in an energy representation in which \mathcal{H}_a and \mathcal{H}_f are diagonal. The basis states will be denoted by $|an\rangle$, where a refers to the state of the atom and n refers to the excitation state of the radiation field oscillator, or the number of photons present. Thus the matrix elements of \mathcal{H}_a and \mathcal{H}_f are:*

*This matrix representation for treating the quantized field was suggested by a National Bureau of Standards Technical Report by M. Mizushima (unpublished).

$$\langle \alpha n | \mathcal{H}_a | \beta m \rangle = E_a \delta_{\alpha\beta} \delta_{mn}$$

$$\langle \alpha n | \mathcal{H}_f | \beta m \rangle = n\omega \delta_{\alpha\beta} \delta_{mn}$$

We are neglecting the zero-point energy of the field.

For \mathcal{H}_i we will assume the form of a product of an operator on the atomic system with an operator on the oscillator. The latter operator will be linear in the creation and annihilation operators for the oscillator, so that \mathcal{H}_i has matrix elements only between states which differ by one in photon number. The usual electromagnetic interactions $\vec{p} \cdot \vec{A}$ or $\vec{\mu} \cdot \vec{H}$ are of this form.

As in the previous work we shall concentrate on the simple case of two atomic states. Let \mathcal{H}_i have only symmetric off diagonal elements with respect to the two atomic states. Then its matrix elements are:

$$\langle \alpha n | \mathcal{H}_i | \beta n + 1 \rangle = \langle \beta n | \mathcal{H}_i | \alpha n + 1 \rangle = c_n = c_n^*$$

The details of the interaction are all consolidated into the letter c_n . We note only that the matrix elements of the creation and annihilation operators, and hence the c_n , are proportional to $(n+1)^{1/2}$. We can now write down a sample portion of the infinite matrix representation for

\mathcal{H}_Q :

$$\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & E_a + (n-1)\omega & 0 & 0 & c_n^{-1} & 0 & 0 & \cdot \\ \cdot & 0 & E_\beta + (n-1)\omega & c_n^{-1} & 0 & 0 & 0 & \cdot \\ \cdot & 0 & c_n^{-1} & E_a + n\omega & 0 & 0 & c_n & \cdot \\ \cdot & c_n^{-1} & 0 & 0 & E_\beta + n\omega & c_n & 0 & \cdot \\ \cdot & 0 & 0 & 0 & c_n & E_a + (n+1)\omega & 0 & \cdot \\ \cdot & 0 & 0 & c_n & 0 & 0 & E_\beta + (n+1)\omega & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

This has a familiar look to it. If c were independent of n , and if n extended to $-\infty$ instead of just to zero, we would have exactly the Floquet Hamiltonian associated with equations 1 and shown in equation 22. For large n , c_n varies slowly with n . Then if we let n_0 be some very large photon number, we can make an approximate identification:

$$\mathcal{H}_Q \approx n_0 \omega 1 + \mathcal{H}_F \quad (67)$$

where we use c_{n_0} for c in \mathcal{H}_F . The identification is good only for photon numbers near n_0 , but improves as n_0 increases.

In writing equation 67 we are also associating the basis states for the two matrix representations. We are saying that the quantum state $|an_0 + m\rangle$ is approximately isomorphic to the Floquet state $|am\rangle$ of chapter VI. This isomorphism is very good for $n_0 \gg m$. Of course it becomes nonsense for $m < -n_0$ since we no longer have any quantum states to correspond to the Floquet states. As we vary the strength of the field we are changing n_0 , and hence changing the correspondence between

quantum and Floquet states. Then too quantum states can be looked at in a coordinate representation as a product of a wave function for the atom with a wave function for the oscillator, a concept we did not have for the Floquet states. Thus the correspondence of the abstract Floquet states with quantized field states is a rather limited one. Nevertheless it is sufficient to permit an interpretation of the transition probability equations of chapter VI from a quantized field view point.

First we shall try to reconstruct the amplitude functions $U_{\beta\alpha}(t;t_0)$ appearing in the solution of the semi-classical Schrödinger equation 17 in terms of states of the quantized field. $U_{\beta\alpha}$ contains no detailed information about the radiation field, since the field is considered classical and unchanged by its interaction with an atom. So we must first find a state of the quantized field which as closely as possible approximates the classical behavior of the field appearing in \mathcal{H}_C . Such a state is the so-called oscillating wave packet (Ref. 3, pp. 67-69). In terms of energy eigenstates it can be written

$$\psi(\xi, t) = \sum_{n=0}^{\infty} A_n e^{-in\omega t} |n\rangle \quad (68)$$

where the states $|n\rangle$ are the Hermite orthogonal functions with ξ as a variable, and the coefficients are

$$A_n = \frac{\xi_0^n e^{-\frac{1}{4}\xi_0^2}}{(2^n n!)^{1/2}} \quad (69)$$

where ξ_0 is the classical amplitude of the field. This state has the

property that the expectation value of the coordinate ξ is just that of a classical oscillator:

$$\langle \xi \rangle = \xi_0 \cos \omega t$$

Since this is the time dependence of the field used in \mathcal{H}_C , we shall use the oscillating wave packet to represent the classical field in terms of quantum states.

Suppose then we represent the initial state of the system by

$$|t_0\rangle = \sum_n A_n e^{-in\omega t_0} |an\rangle$$

which we interpret as atomic state a at time t_0 plus a classical field.

We let this state evolve in time according to the quantized field

Hamiltonian \mathcal{H}_Q . The probability that at time t it will be in the atomic state β with the classical field still present is then

$$\langle t_f | e^{-i\mathcal{H}_Q(t-t_0)} | t_0 \rangle \quad (70)$$

where

$$|t_f\rangle = \sum_m A_m e^{-im\omega t} |\beta m\rangle$$

This probability is what we would expect to correspond to $U_{\beta a}(t; t_0)$.

In order to make the quantized field really classical we must go to the correspondence limit of large photon numbers. The amplitudes A_n are peaked about photon number $n_0 \approx \frac{1}{2} \xi_0^2$. The width of the peak is about $\xi_0 \approx (2n_0)^{1/2}$. If we make the classical approximation that $n_0 \gg 1$ or $\xi_0 \gg 1$, this peak becomes relatively narrow. The only terms in the sums in $|t_f\rangle$ and $|t_0\rangle$ that are then important are those close

(within a few ξ_0) to n_0 . In this vicinity the c_n in \mathcal{H}_Q can be well approximated by c_{n_0} . So we replace \mathcal{H}_Q in equation 70 by $n_0 \omega 1 + \mathcal{H}_F$. We also replace the quantum states by Floquet states to accommodate the increased range in summation index, defining $A_n = 0$ for $n < 0$. States far from n_0 in photon number are strongly damped by the A coefficients, so it does not much matter whether we neglect them or add more.

Canceling factors of $e^{in_0 \omega t}$ we then have

$$U_{\beta\alpha}(t;t_0) \approx \sum_{nm} A_m^* A_n \langle \beta m | e^{-i \mathcal{H}_F(t-t_0)} | \alpha n \rangle e^{im\omega t} e^{-in\omega t_0} \quad (71)$$

The introduction of \mathcal{H}_F and Floquet states permits us to utilize their periodic properties to rewrite equation 71 in the form

$$U_{\beta\alpha}(t;t_0) \approx \sum_{kn} A_{n+k}^* A_n \langle \beta k | e^{-i \mathcal{H}_F(t-t_0)} | \alpha 0 \rangle e^{ik\omega t}$$

It can be shown that the sum over n is just one plus the order of k^2/n_0 . The matrix elements fall off strongly for large k , hence only values of $k \ll n_0$ are important. So to a good approximation we can replace the n sum by unity and obtain finally

$$U_{\beta\alpha}(t;t_0) = \sum_k \langle \beta k | e^{-i \mathcal{H}_F(t-t_0)} | \alpha 0 \rangle e^{ik\omega t}$$

This agrees with equation 26 in chapter VI. If we now differentiate this equation with respect to t we shall find that U satisfies the Schrödinger equation 18 with the Hamiltonian \mathcal{H}_C of equation 1 and the same initial conditions. Thus the semi-classical treatment of the radiation field is completely recoverable from the quantum treatment in the approximation of large quantum numbers.

We can now fortify the interpretation of the transition probability equations 28 and 29 of chapter VI. Since the only Floquet states that contribute to the sum over k are those with small k , we can identify them with the real quantized field states of photon number $n_0 + k$. In equation 28 we identify the initial state $|t_0\rangle$ with that given above for equation 70, namely an oscillating wave packet. This represents a field of well defined initial phase, which is exactly what was used in arriving at equation 28. The interpretation of equation 28 can now be read in terms of quantized field states. In equation 29 we used a pure energy eigenstate for an initial condition of the field. For such a state the probability of a given amplitude of the field is independent of time, hence it represents a field of completely undefined phase. The transition probability in equation 29 reflects this in its functional dependence.

The quantized field formalism thus shows us how to interpret transition probabilities as taking place between states of both the atom and the radiation field. These are stationary states when the radiation field is present but not interacting, so may be studied by methods of time-independent quantum mechanics. They permit a more unified picture of many phenomena. For example the double quantum transition discussed in chapter IX can be described as taking place between the quantized field states $|an_0\rangle$ and $|\beta n_0 + 2\rangle$ via the intermediate states $|an_0 + 1\rangle$ or $|\beta n_0 + 1\rangle$. The double quantum transition discussed in chapter IV can also be described as going between the quantized field states $|an_0\rangle$ and $|\beta n_0 + 2\rangle$ via the intermediate state $|\gamma n_0 + 1\rangle$. Both cases involve intermediate states different from the initial and final states. These two examples of double quantum transitions have sometimes been thought to be distinct (Ref. 5, p. 306), but we now see that the only distinction is in the

identification of the intermediate state. Experimentally the distinction of having a third atomic state is significant, because with it we may have less energy non-conservation in the intermediate state than the ω we must have without it. Hence we can often observe double quantum transitions through well-placed intermediate atomic states with much weaker oscillating fields than are otherwise required. The four-quantum transition mentioned in chapter IX would be a mixture of the "two kinds" of multiple quantum transition.

The reality of the eigenstates of H_Q as true stationary states of the atom plus radiation field in interaction was brought out in Autler and Townes "resonant modulation" experiments (1). By observing the absorption of a weak oscillating field at a microwave frequency causing occasional transitions to a far removed state, they were able to observe directly the "spectrum" of a pair of states strongly excited near resonance by a radio frequency field. The positions and strengths of the absorption lines at the microwave frequency were a direct measure of the eigenstates and their relative populations for the pair of levels interacting with the strong rf field. Autler and Townes did not think of this spectrum as corresponding to stationary states because they viewed the field classically. From a quantized field viewpoint, however, we would describe the microwave transitions as taking place between eigenstates of the atom--rf field system plus the microwave field:

$$|\lambda_{an} n' \rangle \rightarrow |\lambda_{ym} n' + 1 \rangle$$

where the n' is the photon number at the microwave frequency. Each resonance absorption would correspond to a superposition of many such transitions which have the same difference between m and n :

$$\omega' = \lambda_{an} - \lambda_{ym} = q_a - q_y + (n-m)\omega$$

but nevertheless transitions between states which are stationary in the absence of the microwave field.

If the $|\lambda_{an}\rangle$ are stationary states, one should not only have induced transitions between them, but also spontaneous transitions. The relevant matrix elements are in general non-zero, so the quantized field formalism does predict such transitions. The semi-classical treatment also gives these spontaneous transitions, since it predicts radiation at the frequency differences $\lambda_{an} - \lambda_{\beta m}$ from the induced moments of the atom at these frequencies, as mentioned at the end of chapter VI. Observation of such transitions depends on the coherence of the spontaneous radiation from many atoms, a problem which we shall not go into here.

One paramount advantage of using a quantized field description is that it is readily extended to include additional frequencies of excitation, something we could not do with the theory of chapter VI. The extension merely requires the addition of another photon number for each additional mode of the radiation field which we wish to consider. If there are a large number of photons in any mode, we can approximate its interaction matrix elements with the atom to make them independent of photon number, just as we did for the single mode at the beginning of this chapter. The resultant interaction is easier to deal with mathematically. This formalism will then provide a medium for handling such problems as frequency mixing and harmonic generation.

If a second frequency of excitation is nonresonant, one of its

principal effects is to shift the energy levels of the atom. This shift can be computed readily from the quantized field formalism and perturbation theory. Suppose atomic states α and β are connected by the matrix elements $2c \cos \omega t + 2b \cos \omega' t$ in the semi-classical Hamiltonian \mathcal{H}_C . The quantized field matrix elements are then

$$\langle \alpha n, n' | \mathcal{H}_i | \beta n+1, n' \rangle = \langle \beta n, n' | \mathcal{H}_i | \alpha n+1, n' \rangle = c = c^*$$

$$\langle \alpha n, n' | \mathcal{H}_i | \beta n, n'+1 \rangle = \langle \beta n, n' | \mathcal{H}_i | \alpha n, n'+1 \rangle = b = b^*$$

where n and n' are the photon numbers at frequencies ω and ω' respectively and the dependence of c and b on these photon numbers has been neglected. From second order perturbation theory the shift in the energy $E_\alpha + n\omega + n'\omega'$ of the state $|\alpha n, n'\rangle$ is

$$\sum_{m, m'}' \frac{|\langle \alpha n, n' | \mathcal{H}_i | \beta m, m' \rangle|^2}{(E_\alpha + n\omega + n'\omega') - (E_\beta + m\omega + m'\omega')} = \frac{c^2}{\omega_0 + \omega} + \frac{b^2}{\omega_0 - \omega'} + \frac{b^2}{\omega_0 + \omega'}, \quad (72)$$

where the prime on the sum means we have omitted the resonant term with the denominator $\omega_0 - \omega$. The energy of $|\beta n+1, n'\rangle$ will be shifted by the same amount in the opposite direction, so that the shift in the resonance frequency is twice that given above (compare equation 66).

If there are also matrix elements connecting α with other atomic levels, we must also sum over these levels in equation 72. For example the matrix element

$$g = \langle \alpha n, n' | \mathcal{H}_i | \gamma n\pm 1, n' \rangle = g^*$$

would contribute to E_α a shift

$$\frac{g^2}{\omega_1 - \omega} + \frac{g^2}{\omega_1 + \omega}$$

where $\omega_1 = E_\alpha - E_\gamma$. This shift would not necessarily be doubled in the resonance frequency since levels β and γ might not be connected by g . These shifts can be thought of as the result of transitions from $|a n, n'\rangle$ to another state, which then decays back to the original state. Since energy is not conserved in the intermediate state, the transition is virtual. In the quantized field formalism the shifts due to additional atomic levels or to additional frequencies of excitation are both produced by this same mechanism and come out of the same perturbation formula, thus explaining the similarity in their form noted in chapter IX.

In quantum field theory, matrix elements such as b are not zero even when n' is zero. A level shift should occur by a spontaneous virtual transition when no radiation at ω' is present. Although the matrix elements may be very small, this shift exists for all modes of the radiation field. The total shift, summed over an infinite number of modes of the field, is infinite. This kind of shift has been the subject of much investigation in the theory of quantum electrodynamics and requires renormalizations to eliminate the divergences. We are here assuming that all that has been done and that any atomic level shifts due to spontaneous virtual transitions, such as the Lamb shift in hydrogen, have been included in \mathcal{H}_a . The shifts we have described here are increases to shifts such as the Lamb shift due to the increased probability of the virtual transition when quanta are already present in the field, i. e. induced virtual transitions. This we believe to be the true explanation for shifts such as the Bloch-Siegert shift.

A number of approximations were made in showing the equivalence of the quantized field formalism and the Floquet formalism of chapter VI. All of these were based on the assumption that the photon number n_o is very large. To show how good an approximation this is we have worked out some order of magnitude estimates for n_o . Both n_o and the x parameter of chapter VIII are dimensionless variables representing in some way the strength of the oscillating field, so there should be a dimensionless number relating them. For the field quantized in a cavity of volume V :

$$c = c_{n_o} = \mu(2\pi n_o/V\omega)^{1/2} = (\omega/2)x$$

or

$$n_o = (\nu V/4\mu^2)x^2$$

where μ is an electric or magnetic moment of the atom and $\nu = \omega/2\pi$. The number of photons hence depends not only on x^2 , but on the frequency, the volume of the cavity, and the properties of the atom. If we take V to be the volume of a resonant cavity whose fundamental mode has frequency ν and choose for μ values typically associated with a natural frequency ν of the atom, then some rough orders of magnitude are:

Near infrared	$\nu = 4 \times 10^{14}$ cps	$n_o = 10^{10} x^2$
Microwave	$\nu = 10^{10}$ cps	$n_o = 10^{22} x^2$
Radio frequency	$\nu = 10^6$ cps	$n_o = 10^{37} x^2$

The photon density varies less violently with frequency:

$$n_o/V = 10^{21} \text{ to } 10^{25} x^2 \text{ photons/cm}^3$$

In all cases except very weak fields the approximation $n_0 \gg 1$ is exceedingly good and one should have no qualms about using a classical description of the field. A simple way to determine when the quantized field mathematics is necessary is to compare the spontaneous radiation lifetime of the states with other relevant times in the experiment.

Since $c_{n_0+m} = c_{n_0} (1 + \frac{m}{n_0})^{1/2} \approx c_{n_0} (1 + \frac{m}{2n_0})$ we can expect deviations in the eigenvalues of \mathcal{H}_Q from those of \mathcal{H}_F to be of relative order m/n_0 and a sample matrix diagonalized on the computer confirms this. This lowest order correction has the effect of decreasing the frequency without destroying the periodicity. Thus the harmonics spontaneously emitted by a system would not be exact harmonics, but would be shifted by the order of x/n_0 . As can be seen from the above figures this shift is too small to worry about, except when x is very small, in which case the spontaneous radiation would doubtless be too weak to observe.

APPENDIX A

PERTURBATION THEORY

We shall describe here a perturbation theory for finding eigenvalues and eigenvectors of hermitian matrices, both for the non-degenerate case, and the case of two nearly degenerate eigenvalues. Although the methods are not original, it was thought convenient to have the formulae available in the form used in the body of this thesis. Also the following derivation brings out the parallel between the non-degenerate and degenerate cases.

Consider the equation

$$(E^0 + V)A = AE \tag{A1}$$

where E^0 and V are given hermitian matrices. We wish to find the diagonal matrix of eigenvalues E and the unitary matrix of eigenvectors A . We shall assume that the unperturbed matrix E^0 is already diagonal and seek solutions in power series in the perturbation V .

We first transpose equation A1

$$AE - E^0 A = VA$$

and then write out its components

$$\sum_k (A_{ik} E_k \delta_{kp} - E_i^0 \delta_{ik} A_{kp}) = \sum_k V_{ik} A_{kp}$$

Solving for the A_{ip} on the left we obtain

$$A_{ip} = \sum_k \frac{V_{ik} A_{kp}}{E_p - E_i^0} \tag{A2}$$

E_p and A_{ip} are the particular eigenvalue and eigenvector we seek. We consider two cases.

Case I: Non-degenerate Eigenvalue

Suppose that $E_p^0 - E_i^0$ is large compared to the components of V for all i except $i = p$. Then from equation A2 we see A_{ip} will be small except for $i = p$. We separate out the large term A_{pp} from the sum over k and write equation A2 as

$$A_{ip} = \frac{V_{ip} A_{pp}}{E_p - E_i^0} + \sum_k' \frac{V_{ik} A_{kp}}{E_p - E_i^0}$$

The prime on the sum means that the term for $k = p$ is to be omitted. Since the last term is smaller, we can solve this implicit equation for A_{ip} by iteration, obtaining

$$A_{ip} = \left[\frac{V_{ip}}{E_p - E_i^0} + \sum_j' \frac{V_{ij} V_{jp}}{(E_p - E_i^0)(E_p - E_j^0)} + \dots \right] A_{pp} \quad (A3)$$

To determine E_p we set $i = p$ in equation A3 and multiply by $(E_p - E_p^0)$. The A_{pp} can be canceled from both sides, leaving the familiar result

$$E_p = E_p^0 + V_{pp} + \sum_i' \frac{V_{pi} V_{ip}}{E_p - E_i^0} + \sum_i' \sum_j' \frac{V_{pi} V_{ij} V_{jp}}{(E_p - E_i^0)(E_p - E_j^0)} + \dots \quad (A4)$$

This is an implicit equation for E_p and is usually evaluated by iteration.

The element A_{pp} is obtained from the normalization of the eigenvector, or unitarity of the A matrix

$$\sum_i |A_{ip}|^2 = 1$$

To second order this gives

$$A_{pp} = 1 - \frac{1}{2} \sum_i' \left| \frac{V_{ip}}{E_p - E_i^0} \right|^2 \quad (A5)$$

The eigenvectors A_{ip} will automatically be orthogonal to other eigenvectors computed by the same method. Equations A3, A4, and A5 provide the complete perturbation solution to equations A2 for a non-degenerate eigenvalue.

Case II: Two-fold Nearly Degenerate Eigenvalues

Suppose that $E_p - E_i^0$ is large compared to the components of V for all i except $i = p$ and q . Then from equation A2 we see A_{ip} will be small except for $i = p$ and q . We separate out the large terms A_{pp} and A_{qp} from the sum over k and write equation A2 as

$$A_{ip} = \frac{V_{ip} A_{pp}}{E_p - E_i^0} + \frac{V_{iq} A_{qp}}{E_p - E_i^0} + \sum_k' \frac{V_{ik} A_{kp}}{E_p - E_i^0}$$

The prime on the sum now means that both the terms for $k = p$ and for $k = q$ are to be omitted. Since the last term is smaller, we can solve this implicit equation for A_{ip} by iteration, obtaining the result

$$\begin{aligned} A_{ip} = & \left[\frac{V_{ip}}{E_p - E_i^0} + \sum_j' \frac{V_{ij} V_{jp}}{(E_p - E_i^0)(E_p - E_j^0)} + \dots \right] A_{pp} \\ & + \left[\frac{V_{iq}}{E_p - E_i^0} + \sum_j' \frac{V_{ij} V_{jq}}{(E_p - E_i^0)(E_p - E_j^0)} + \dots \right] A_{qp} \quad (A6) \end{aligned}$$

To determine E_p we set $i = p$ in equation A6 and multiply by $(E_p - E_p^0)$. But the A_{pp} can not be canceled from both sides because of the A_{qp} terms in equation A6. We are left with

$$E_p A_{pp} = E_p^0 A_{pp} + \mathcal{V}_{pp}(E_p) A_{pp} + \mathcal{V}_{pq}(E_p) A_{qp}$$

where

$$\mathcal{V}_{pp}(E) = V_{pp} + \sum_i' \frac{V_{pi} V_{ip}}{E - E_i^0} + \sum_i' \sum_j' \frac{V_{pi} V_{ij} V_{jp}}{(E - E_i^0)(E - E_j^0)} + \dots$$

and

(A7)

$$\mathcal{V}_{pq}(E) = V_{pq} + \sum_i' \frac{V_{pi} V_{iq}}{E - E_i^0} + \sum_i' \sum_j' \frac{V_{pi} V_{ij} V_{jq}}{(E - E_i^0)(E - E_j^0)} + \dots$$

We need another equation relating A_{pp} and A_{qp} . To obtain it we merely set $i = q$ in equation A6 and multiply by $(E_p - E_q^0)$. We find

$$E_p A_{qp} = E_q^0 A_{qp} + \mathcal{V}_{qp}(E_p) A_{pp} + \mathcal{V}_{qq}(E_p) A_{qp}$$

where $\mathcal{V}_{qp}(E)$ and $\mathcal{V}_{qq}(E)$ are defined by relations exactly analogous to equations A7. These two equations for A_{pp} and A_{qp} can be combined into a single matrix equation

$$\begin{pmatrix} E_p^0 + \mathcal{V}_{pp}(E) & \mathcal{V}_{pq}(E) \\ \mathcal{V}_{qp}(E) & E_q^0 + \mathcal{V}_{qq}(E) \end{pmatrix} \begin{pmatrix} A_{pp} \\ A_{qp} \end{pmatrix} = E \begin{pmatrix} A_{pp} \\ A_{qp} \end{pmatrix} \quad (A8)$$

This is an implicit eigenvalue equation for the two eigenvalues E_p and E_q . However the distinction between E_p and E_q in the \mathcal{V} matrix

elements is only a third order effect.

The hermiticity of V guarantees the hermiticity of $V(E)$, hence we can always diagonalize the above matrix. The eigenvalues are

$$E = \frac{1}{2} [E_p^0 + \gamma_{pp}(E) + E_q^0 + \gamma_{qq}(E)] \pm \frac{1}{2} \{ [E_p^0 + \gamma_{pp}(E) - E_q^0 - \gamma_{qq}(E)]^2 + 4|\gamma_{pq}|^2 \}^{1/2} \quad (A9)$$

If E_p denotes the larger root, the dominant eigenvector components are

$$\begin{aligned} A_{pp} &= N e^{i\theta} \left[\frac{1 + R(E_p)}{2} \right]^{1/2} \\ A_{qp} &= N \left[\frac{1 - R(E_p)}{2} \right]^{1/2} \\ A_{pq} &= N e^{i\theta} \left[\frac{1 - R(E_q)}{2} \right]^{1/2} \\ A_{qq} &= -N \left[\frac{1 + R(E_q)}{2} \right]^{1/2} \end{aligned} \quad (A10)$$

where θ is the phase angle of γ_{pq} and

$$R(E) = [E_p + \gamma_{pp}(E) - E_q - \gamma_{qq}(E)] \{ [E_p + \gamma_{pp}(E) - E_q - \gamma_{qq}(E)]^2 + 4|\gamma_{pq}(E)|^2 \}^{-1/2}$$

N is a normalization constant equal to one minus second order corrections from the other components. The signs guarantee orthogonality.

Equations A6 through A10 provide a complete perturbation solution to equations A2 for two-fold nearly degenerate eigenvalues. These results are essentially the same as those given by Salwen (19, Sec. 3B), although the presentation and notation are different.

The same procedure could evidently be extended to any number of nearly degenerate eigenvalues. However it becomes less useful as an approximation because of the increased analytical difficulty of exactly diagonalizing larger than two by two matrices.

APPENDIX B

THE CHARACTERISTIC EXPONENT FROM INFINITE DETERMINANTS

We have mentioned in Chapter VI that the characteristic exponents for the Schrödinger equation with a harmonic perturbation are in principle obtained from the characteristic equation $\det (\mathcal{H}_F - \lambda \mathbf{1}) = 0$. We shall in this Appendix show how this determinantal equation can actually be evaluated to find the series expansion for the characteristic exponent given in equation 56. We use the dimensionless notation of Chapter VIII, with \mathcal{H}_F given by equation 42. As it stands the value of $\det (\mathcal{H}_F - \lambda \mathbf{1})$ must be infinite, since the product of the diagonal elements diverges. To obtain a convergent determinant we divide each row of $(\mathcal{H}_F - \lambda \mathbf{1})$ by its diagonal element, forming the infinite determinant

$$D(x, y, \lambda) = \begin{vmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \frac{x}{-3-y-\lambda} & 0 & 0 & 0 & \cdot \\ \cdot & \frac{x}{-1+y-\lambda} & 1 & \frac{x}{-1+y-\lambda} & 0 & 0 & \cdot \\ \cdot & 0 & \frac{x}{1-y-\lambda} & 1 & \frac{x}{1-y-\lambda} & 0 & \cdot \\ \cdot & 0 & 0 & \frac{x}{3+y-\lambda} & 1 & \frac{x}{3+y-\lambda} & \cdot \\ \cdot & 0 & 0 & 0 & \frac{x}{5-y-\lambda} & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \quad (B1)$$

By a theorem of St. Bobr (39) the determinant D can be shown to be absolutely convergent for all complex values of x , y , and λ except those producing a zero denominator. The characteristic equation $\det (\mathcal{H}_F - \lambda \mathbf{1}) = 0$ then has the roots $\lambda = z(x, y)$ determined by $D(x, y, z) = 0$.

By exact analogy to the method given in Whittaker and Watson for the Hill determinant (40) we can completely determine the dependence of D on λ in terms of elementary functions. The absolute convergence of D implies that D is an analytic function of λ , except for simple poles at $\lambda = 4n - 1 + y$ and $4n + 1 - y$, n any integer. By changing the sign of all denominators and writing D in reverse order it can be seen that D is an even function of λ . D is also a periodic function of λ with period 4, since adding 4 to z only shifts the center of the determinant, but relative to infinitely remote corners. Because of the periodicity and evenness the residues of D at all its poles must be the same. Now the trigonometric function $\cot \frac{\pi(\lambda + 1 - y)}{4} - \cot \frac{\pi(\lambda - 1 + y)}{4}$ is also an even periodic function of λ with period 4 and simple poles at $4n - 1 + y$ and $4n + 1 - y$, all with residue $+1$. If $K(x, y)$ is the residue of the poles of D , then the function

$$D(x, y, \lambda) - K \left[\cot \frac{\pi(\lambda + 1 - y)}{4} - \cot \frac{\pi(\lambda - 1 + y)}{4} \right]$$

is entire, since all the poles cancel out. As λ approaches infinity along any line not parallel to the real axis the off diagonal elements of D vanish, so that D approaches 1, while the cotangents cancel each other. Thus the above function approaches 1 as λ approaches infinity. An entire function which is everywhere bounded is a constant. Therefore the above function equals one for all λ , or

$$D(x, y, \lambda) = 1 + 2K \frac{\cos \frac{\pi y}{2}}{\cos \frac{\pi \lambda}{2} - \sin \frac{\pi y}{2}} \quad (B2)$$

We can evaluate K in terms of D at any special value of λ . Suppose we set $\lambda = 1$ in equation B2. Then substituting the resultant value for K back into equation B2 we obtain the result

$$D(x, y, \lambda) = \frac{\cos \frac{\pi\lambda}{2} - D(x, y, 1) \sin \frac{\pi y}{2}}{\cos \frac{\pi\lambda}{2} - \sin \frac{\pi y}{2}}$$

To find the characteristic exponent z we have now to solve $D(x, y, z) = 0$, or

$$\cos \frac{\pi z}{2} = D(x, y, 1) \sin \frac{\pi y}{2} \quad (B3)$$

We have thus reduced the problem to the evaluation of an infinite determinant depending on only two variables.

A tridiagonal determinant, such as we have in equation B1, has the property that in its expansion each off diagonal element always appears multiplied by its "partner" located diagonally opposite it on the other side of the main diagonal. Hence the value of the determinant is unchanged if an off diagonal element trades places with its partner, if both change sign, if both are replaced by their geometric mean (symmetrization of the determinant) or if all of one partner is transferred to the other, leaving a factor one behind. Assuming the latter done for each pair of off diagonal elements we can write a tridiagonal determinant as

$$D(\beta) = \begin{vmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \beta_{-2} & 0 & 0 & 0 & 0 & \cdot \\ \cdot & 1 & 1 & \beta_{-1} & 0 & 0 & 0 & \cdot \\ \cdot & 0 & 1 & 1 & \beta_0 & 0 & 0 & \cdot \\ \cdot & 0 & 0 & 1 & 1 & \beta_1 & 0 & \cdot \\ \cdot & 0 & 0 & 0 & 1 & 1 & \beta_2 & \cdot \\ \cdot & 0 & 0 & 0 & 0 & 1 & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \quad (B4)$$

Let us expand $D(\beta)$ by the usual rule for expanding determinants. We start with the product of all the diagonal elements, which is unity. We then consider replacing one diagonal element by an off diagonal element, finding that we must also take its partner. We thus obtain a term $-\beta_n$. We can do this for every off diagonal element so we get the sum of all β_n . We next consider terms containing two β 's. We get all such combinations where the two β 's are distinct and not adjacent. If we try to take two adjacent β 's we cannot take their partners, but must instead take all the β 's. In a finite tridiagonal determinant this product of β 's is multiplied by a zero in a far corner. In a convergent infinite determinant the infinite product of β 's diverges to zero. So such terms need not be considered. Our expansion in general then consists of all possible terms containing a product of a finite number of β 's with the selection rule that no two β 's in the same term can be adjacent. We can write it as follows:

$$D(\beta) = 1 - \sum_{i=-\infty}^{\infty} \beta_i + \sum_{i=-\infty}^{\infty} \sum_{j=i+2}^{\infty} \beta_i \beta_j - \sum_{i=-\infty}^{\infty} \sum_{j=i+2}^{\infty} \sum_{k=j+2}^{\infty} \beta_i \beta_j \beta_k + \dots \quad (B5)$$

For $D(x, y, 1)$ we have

$$\beta_{2n} = \frac{x^2}{(4n+y)(4n-2-y)}, \quad \beta_{2n+1} = \frac{x^2}{(4n+y)(4n+2-y)} \quad (B6)$$

The single sum of β_i from minus to plus infinity can be evaluated by contour integration. The method is described in Titchmarsh (41) and other books on complex variable theory. However in the multiple sums, as written above, we need to sum from an arbitrary, but finite lower limit. Although this sum for β alone can be expressed in terms of the logarithmic derivative of the gamma function, this is of little help in evaluating the multiple sums, let alone summing the β series to obtain D . The evaluation of D can be done analytically if both factors in the denominator of β_i contain y with the same sign. However this corresponds to the physically uninteresting case of degenerate levels, which could have been solved exactly by other methods as well.

An alternative way of evaluating equation B5 is to consider powers of the single sum over β . They will contain among their cross products all the terms we need for the multiple sums, plus a few we do not need. The latter contain powers of a single β_i and products of adjacent β 's. Their sums can be evaluated by the contour integration method and subtracted out. Let us define

$$S_k = \sum_i (\beta_i)^k, \quad S_{kl} = \sum_i (\beta_i)^k (\beta_{i+1})^l, \quad \text{etc.}$$

where each sum is from minus to plus infinity. Then the expansion in equation B5 can be written as

$$\begin{aligned} D(\beta) = & 1 - S_1 + \left(\frac{1}{2} S_1^2 - \frac{1}{2} S_2 - S_{11} \right) \\ & - \left(\frac{S_1^3}{6} + \frac{S_3}{3} + S_{21} + S_{12} + S_{111} - \frac{1}{2} S_2 S_1 - S_{11} S_1 \right) + \dots \quad (B7) \end{aligned}$$

We shall illustrate the use of this equation by evaluating $D(x, y, 1)$ to fourth order in x (second order in β).

Let $a_n = (n + \frac{1}{4} y)^{-1}$ and $b_n = (n - \frac{1}{2} - \frac{1}{4} y)^{-1}$. Then $\beta_{2n} = (\frac{x^2}{16}) a_n b_n$ and $\beta_{2n+1} = (\frac{x^2}{16}) a_n b_{n+1}$. The product of a and b can be rewritten in terms of their difference:

$$a_n b_n = \frac{2}{y+1} (b_n - a_n), \quad a_n b_{n+1} = \frac{2}{y-1} (b_{n+1} - a_n)$$

Thus the sum over β becomes

$$\begin{aligned} S_1 &= \sum_n (\beta_{2n} + \beta_{2n+1}) \\ &= \frac{x^2}{16} \sum_n \left[\frac{2}{y+1} (b_n - a_n) + \frac{2}{y-1} (b_{n+1} - a_n) \right] \end{aligned}$$

Because of the infinite range of the summation index, the sums over b_n and b_{n+1} are identical

$$S_1 = \frac{x^2}{4} \frac{y}{y^2-1} \sum_n (b_n - a_n)$$

The sums are evaluated by contour integration, or recognized as the partial fraction expansion of the cotangent

$$\sum_n a_n = \pi \cot \frac{\pi y}{4}, \quad \sum_n b_n = -\pi \cot \frac{\pi(y+2)}{4} = \pi \tan \frac{\pi y}{4}$$

The final expression for S_1 is

$$S_1 = -\frac{\pi}{2} \frac{x^2 y}{y^2 - 1} \cot \frac{\pi y}{2}$$

For the next order we must evaluate S_2 and S_{11} :

$$S_2 = \sum_n \beta_n^2, \quad S_{11} = \sum_n \beta_n \beta_{n+1}$$

As before we express the β 's in terms of the a 's and b 's and expand the products in partial fractions, obtaining

$$S_2 = \frac{x^4}{256} \left\{ \left[\frac{4}{(y+1)^2} + \frac{4}{(y-1)^2} \right] \sum_n (b_n^2 + a_n^2) - \left[\frac{8}{(y+1)^3} + \frac{8}{(y-1)^3} \right] \sum_n (b_n - a_n) \right\}$$

The sum over the squares of a and b involve second order poles and lead to cosecant squared terms:

$$\sum_n a_n^2 = \pi^2 \csc^2 \frac{\pi y}{4}, \quad \sum_n b_n^2 = \pi^2 \csc^2 \frac{\pi(y+2)}{4} = \pi^2 \sec^2 \frac{\pi y}{4}$$

After simplification we obtain

$$S_2 = \left[\frac{y^2+1}{(y^2-1)^2} \frac{\pi}{8} \csc^2 \frac{\pi y}{2} + \frac{y^3+3y}{(y^2-1)^3} \frac{\pi}{4} \cot \frac{\pi y}{2} \right] x^4$$

and

$$S_{11} = \left[\frac{1}{y^2-1} \frac{\pi^2}{16} \csc^2 \frac{\pi y}{2} + \frac{y}{(y^2-1)^2} \frac{\pi}{4} \cot \frac{\pi y}{2} \right] x^4$$

When we combine all the x^4 terms together we discover that the cotangent squared terms from S_1^2 and the cosecant squared terms from S_2 and S_{11} just counteract each other, leaving a non-trigonometric term

$$\frac{1}{2} S_1^2 - \frac{1}{2} S_2 - S_{11} = \left[\frac{-y^2}{(y^2-1)^2} \frac{\pi^2}{8} - \frac{y(3y^2+1)}{(y^2-1)^3} \frac{\pi}{8} \cot \frac{\pi y}{2} \right] x^4 \quad (B8)$$

This cancellation could have been predicted, for $D(x, y, 1)$ has only simple poles in y at the even integers. These poles are represented by the cotangent function. A cotangent squared term would represent second order poles, which do not occur because of the limitation on the products of β 's that can be formed. At first glance there might appear to be third order poles in equation B8 at $y = \pm 1$, but the cotangent has zeros there, reducing them to second order, and the non-trigonometric term is of just such a size as to cancel the second order poles leaving just first order poles. If we go to higher orders with the expansion of equation B7, we get higher order poles in the sums which must all cancel when the sums are combined in each order. Hence it appears we would be doing too much work.

We can write $D(x, y, 1) = f(x, y) + g(x, y) \cot \frac{\pi y}{2}$, where all the poles are represented by the cotangent. Then substituting into equation B3 we find that the poles disappear and $\cos \frac{\pi z}{2}$ is an entire function of

y as required by the differential equation.

$$\cos \frac{\pi z}{2} = f(x, y) \sin \frac{\pi y}{2} + g(x, y) \cos \frac{\pi y}{2}$$

If we expand f and g in power series in x with coefficients f_{2n} and g_{2n} , then to order x^4 we have found so far

$$\begin{aligned} f_0 &= 1 & g_0 &= 0 \\ f_2 &= 0 & g_2 &= \frac{\pi}{2} \frac{y}{y^2-1} \\ f_4 &= -\frac{\pi^2}{8} \frac{y^2}{(y^2-1)^2} & g_4 &= -\frac{\pi}{8} \frac{y(3y^2+1)}{(y^2-1)^3} \end{aligned}$$

Note that $f_4 = -\frac{1}{2} (g_2)^2$. We surely have done too much work.

If we let $z(x, y) = 1 - y - \varphi(x, y)$, then

$$\cos \frac{\pi z}{2} = \cos \frac{\pi \varphi}{2} \sin \frac{\pi y}{2} + \sin \frac{\pi \varphi}{2} \cos \frac{\pi y}{2}$$

or f and g are related by $f^2 + g^2 = 1$. From our value of g we can in turn write the expansion of φ :

$$\varphi(x, y) = \frac{y}{y^2-1} x^2 - \frac{y}{4} \frac{3y^2+1}{(y^2-1)^3} x^4 + \dots$$

We now have the terms through order x^4 in the expansion of z given in Chapter VIII equation 56. By considering how the products of a and b develop in the various sums in S one can arrive at the powers involved in the partial fraction expansion of z (equation 53). For instance the first terms with $3 + y$ in the denominator come from S_{111} where the products of a's and b's involve factors like $a_{n-1} b_{n+1} = \frac{2}{y+3} (b_{n+1} - a_{n-1})$.

These terms then do not arise until sixth order in x . One is then led to continue to higher orders by postulating the partial fraction expansion, rather than continuing the expansion in equation B7.

Our investigation of an expansion for z via infinite determinants has thus led us back toward the method of undetermined coefficients in a partial fraction expansion used in Chapter VIII. However we no longer need the continued fraction expansion in postulating the partial fraction expansion in equation 53. Both the continued fraction and the tridiagonal determinant are associated with three term recursion relations such as we have in equation 44. When we have more complicated recursion relations, as we would have with the problems discussed in Chapter IX, we can no longer use continued fractions, but can write the infinite determinant. The expansion of an infinite determinant that has more off diagonal elements than a tridiagonal one, is more complex than equation B5, but can still be written down. The general formula for the expansion is given in Hill's famous paper on the motion of the lunar perigee (42). Although mathematicians have worked out convergence criteria for infinite determinants, the original work of Hill seems to be the most advanced work available on their analytical evaluation.

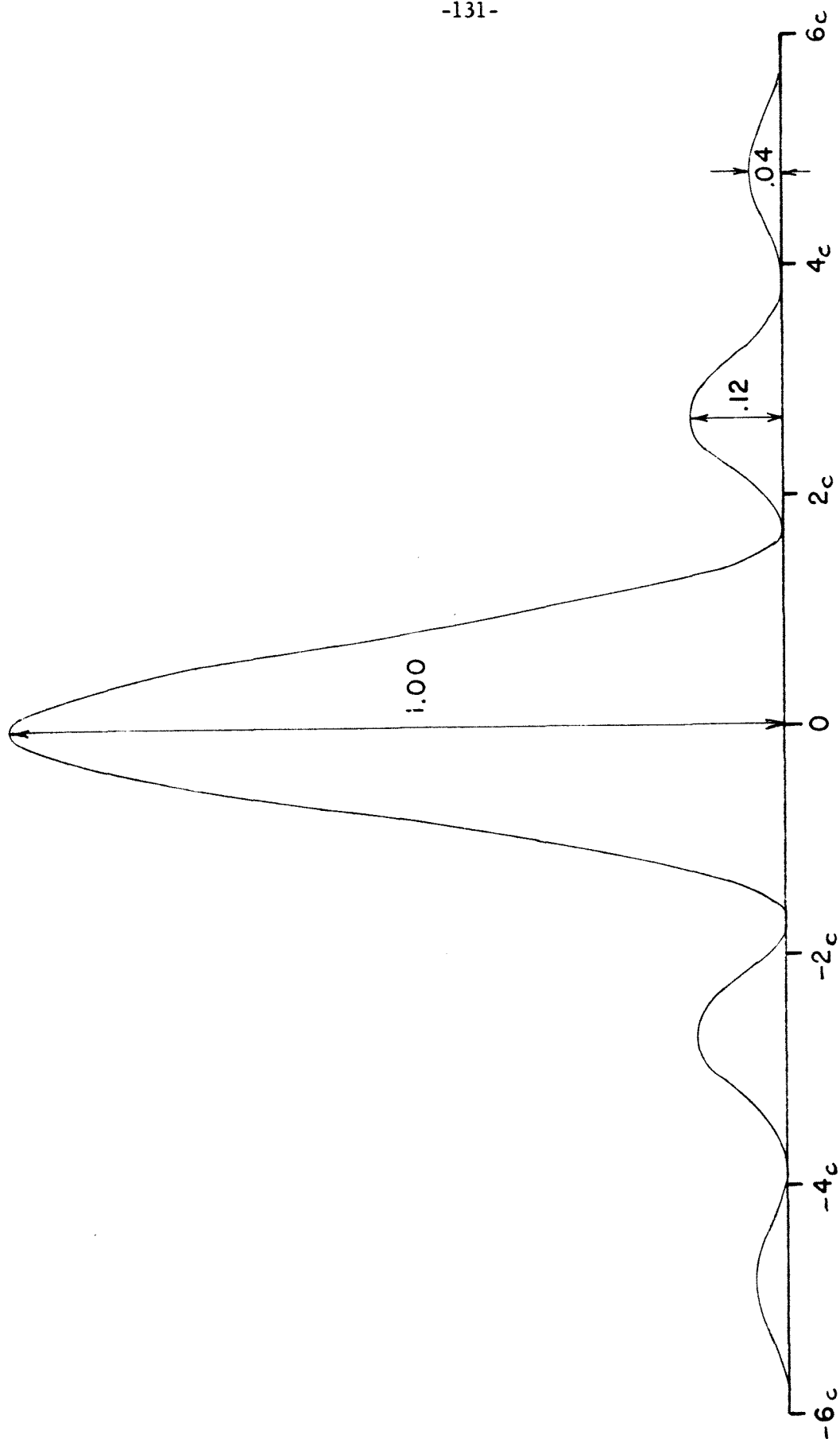


Figure 1. Rabi line shape (equation 3) as a function of $\Delta = \frac{1}{2}(\omega - \omega_0)$ for $ct = \pi/2$.

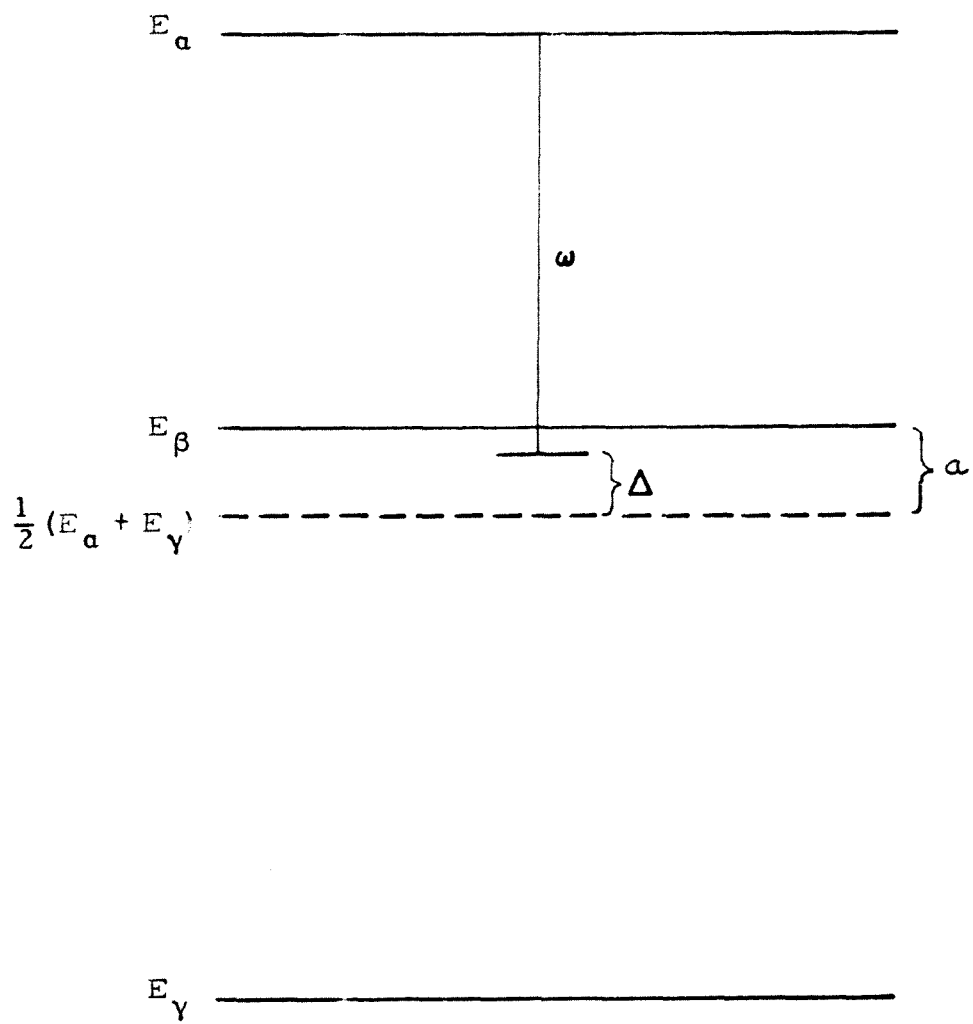


Figure 2. Energy levels and parameters for a three-state system.

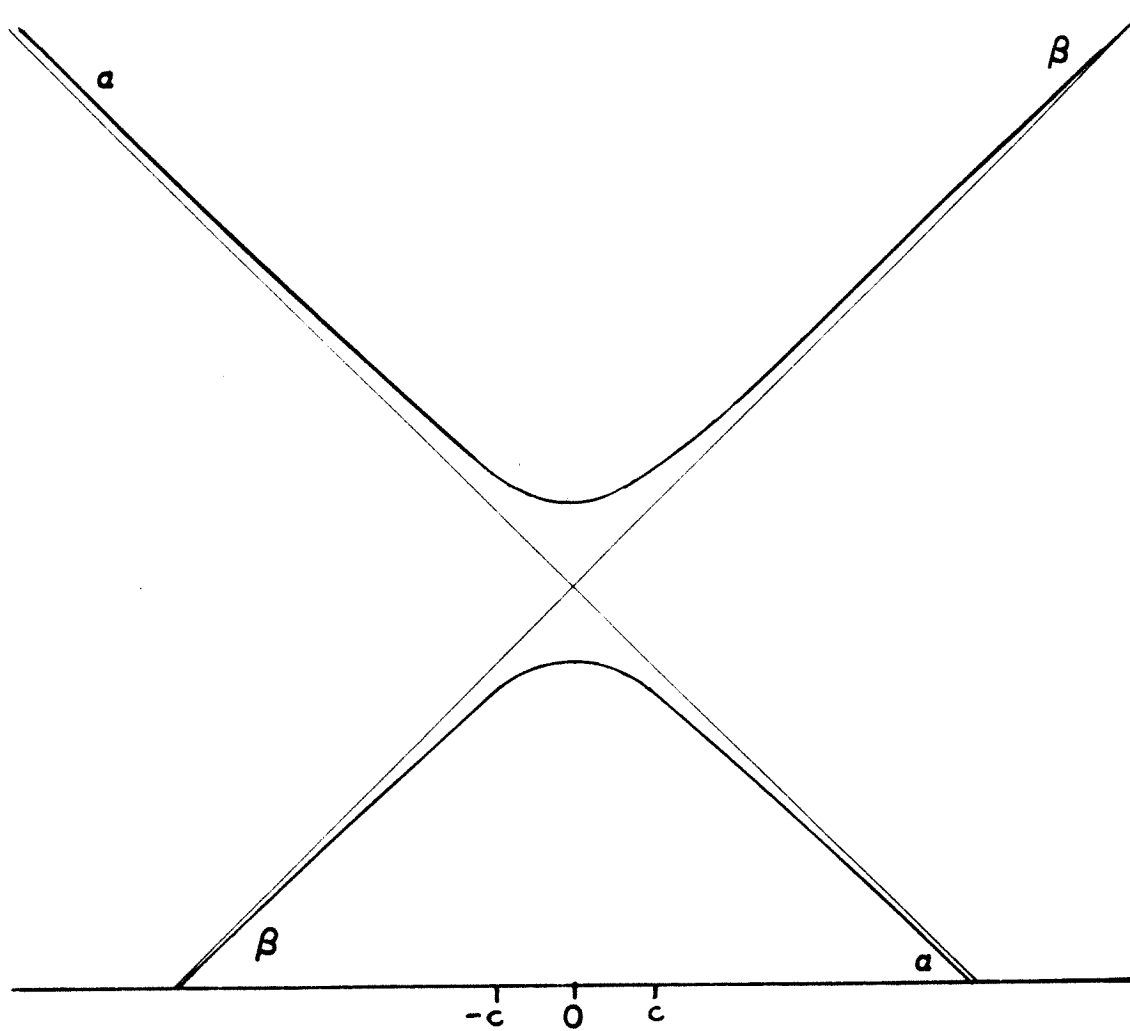


Figure 3. Eigenvalues and diagonal elements of a two-state system as a function of frequency deviation Δ .

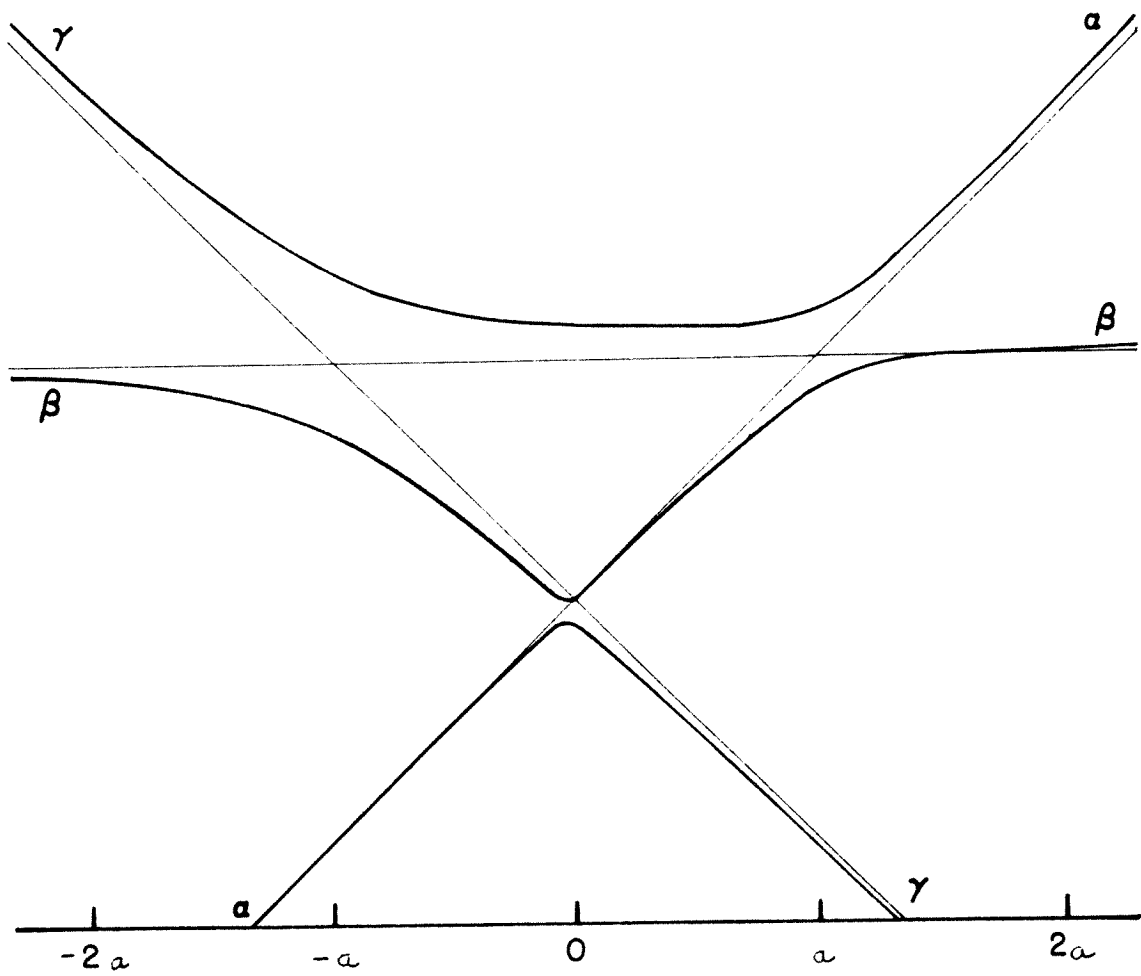


Figure 4. Eigenvalues and diagonal elements of a three-state system as a function of frequency deviation Δ .

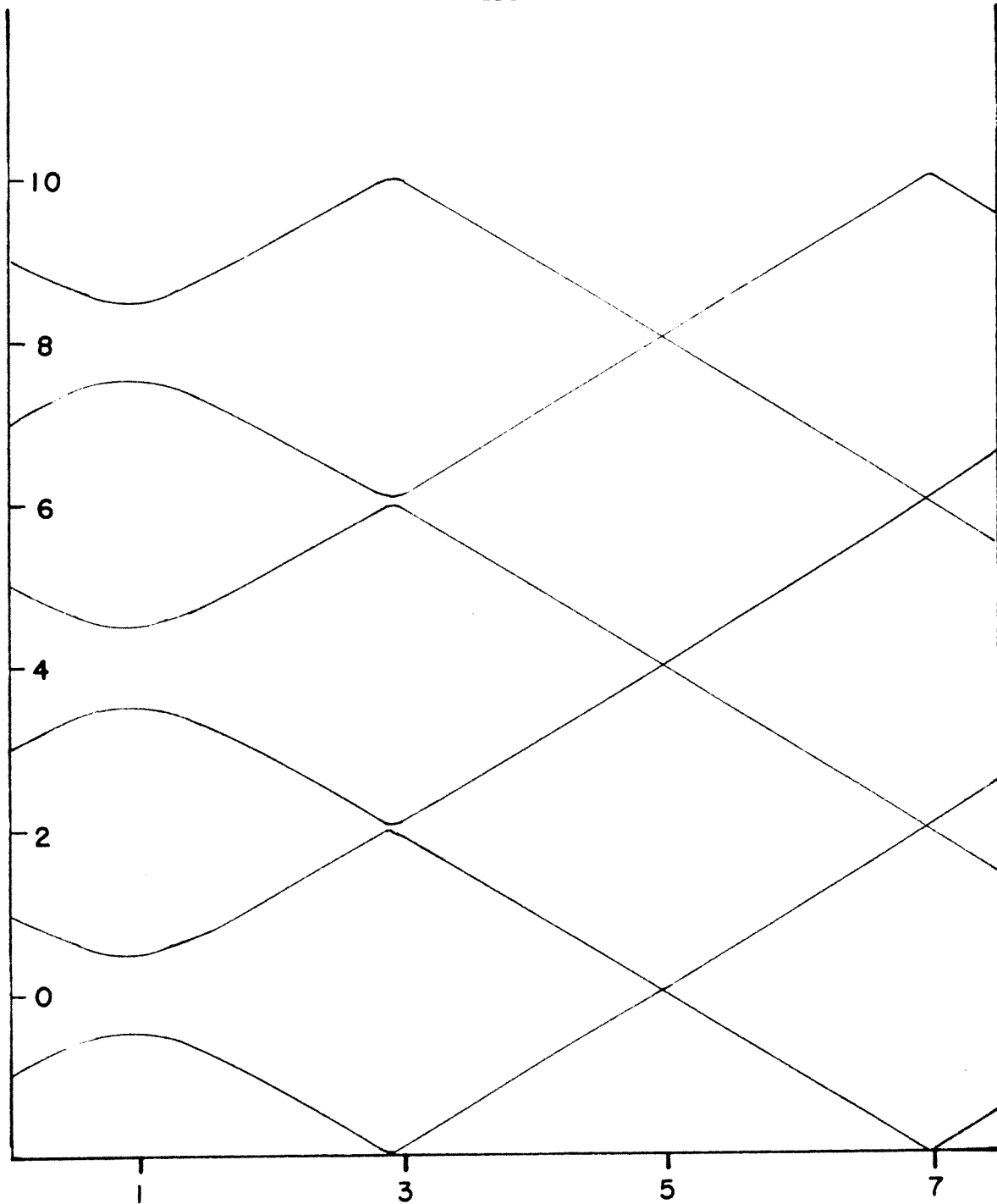


Figure 5. Characteristic exponent z as a function of y showing six branches. $x = 1/2$.

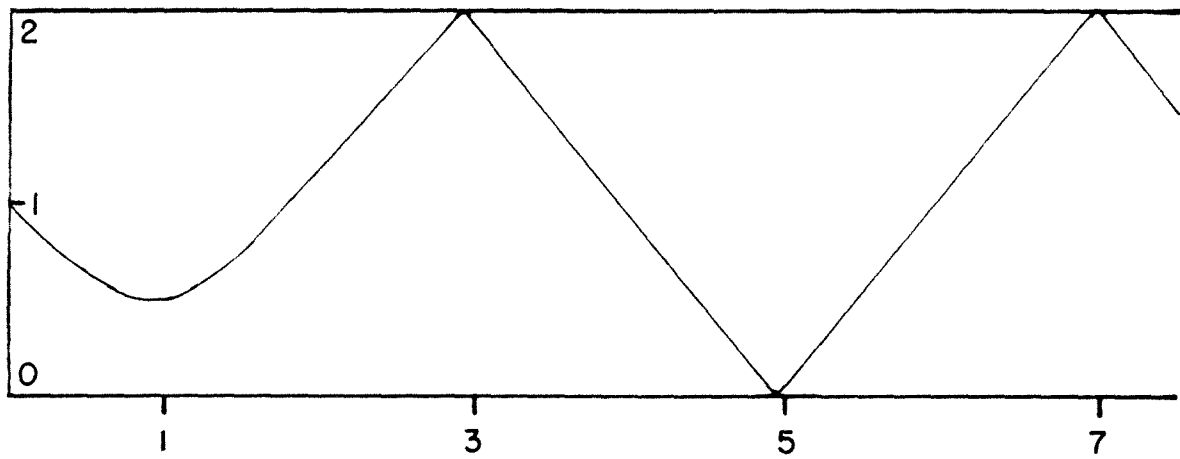


Figure 6a. Characteristic exponent z as a function of y for $x = 1/2$.

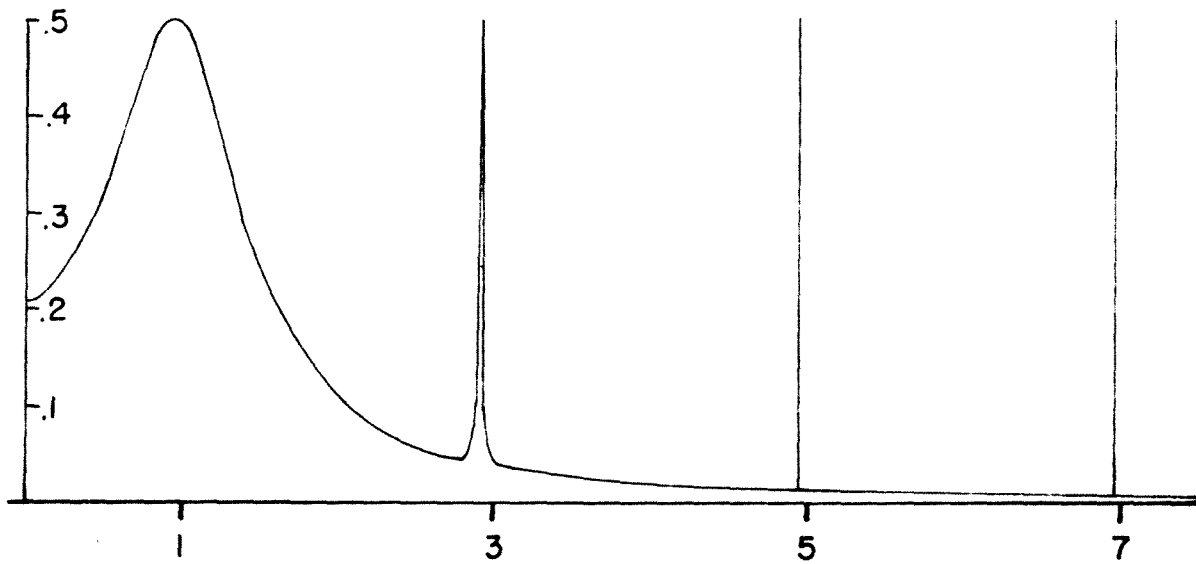


Figure 6b. Average transition probability as a function of y (ω_0) for $x = 1/2$ ($c = 1/4$, $\omega = 1$).

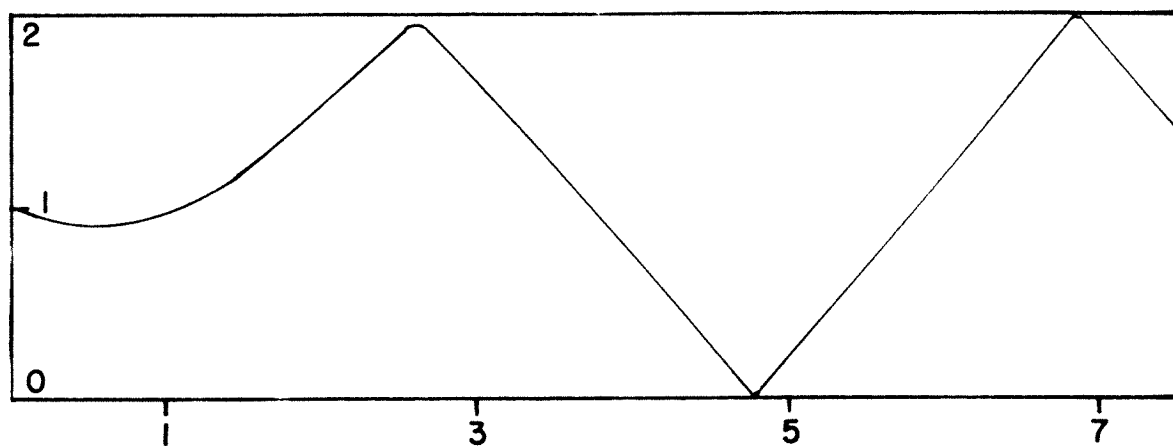


Figure 7a. Characteristic exponent z as a function of y for $x = 1$.

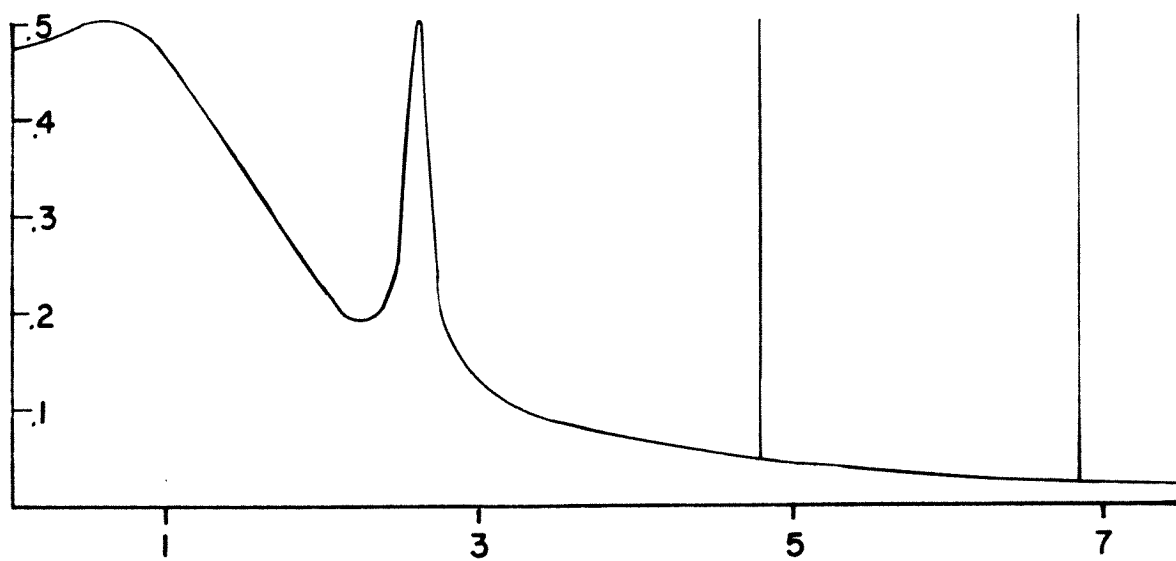


Figure 7b. Average transition probability as a function of y for $x = 1$.

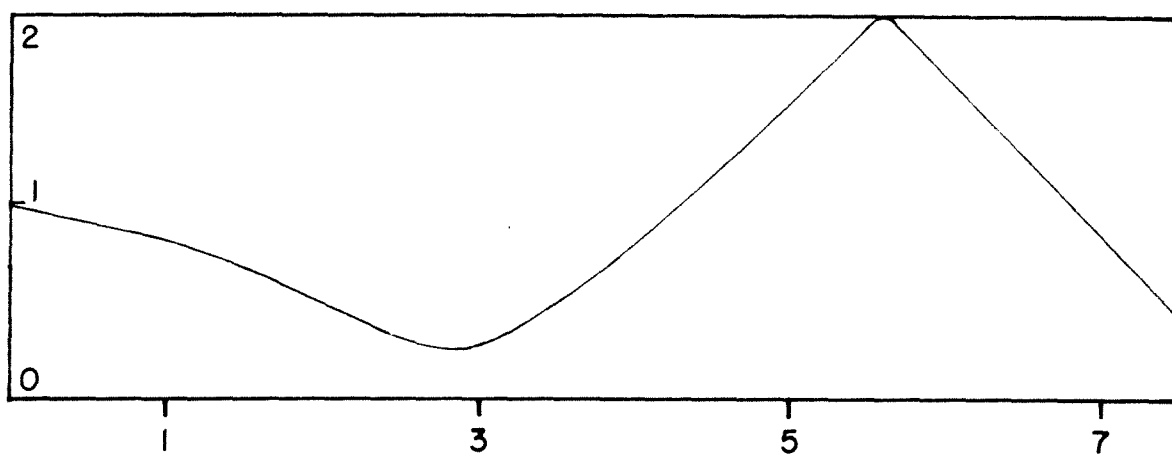


Figure 8a. Characteristic exponent z as a function of y for $x = 3$.

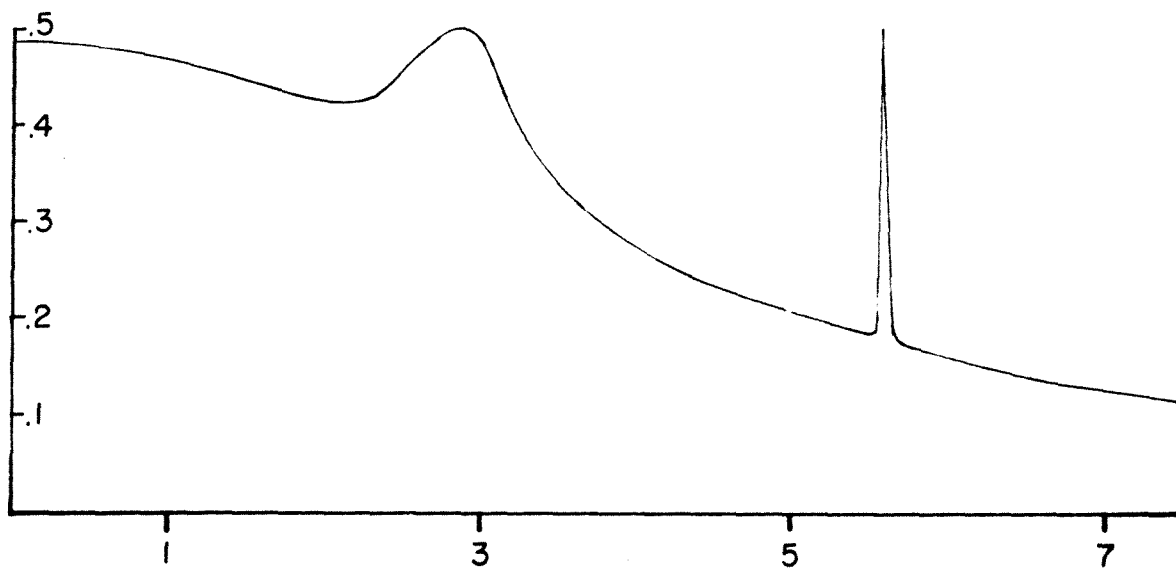


Figure 8b. Average transition probability as a function of y for $x = 3$.

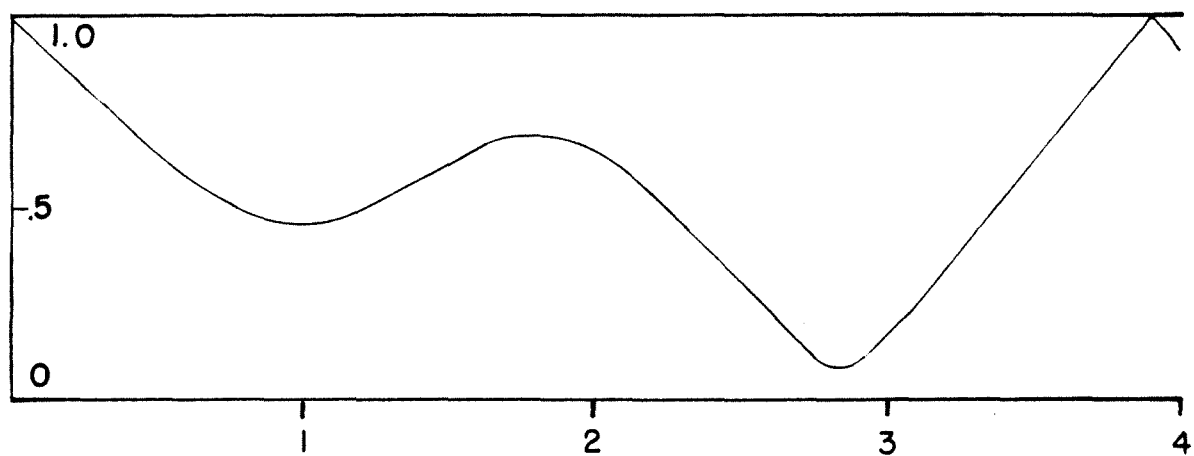


Figure 9a. Characteristic exponent z as a function of y for $w = x = x' = 0.6$, $\delta = 0$.

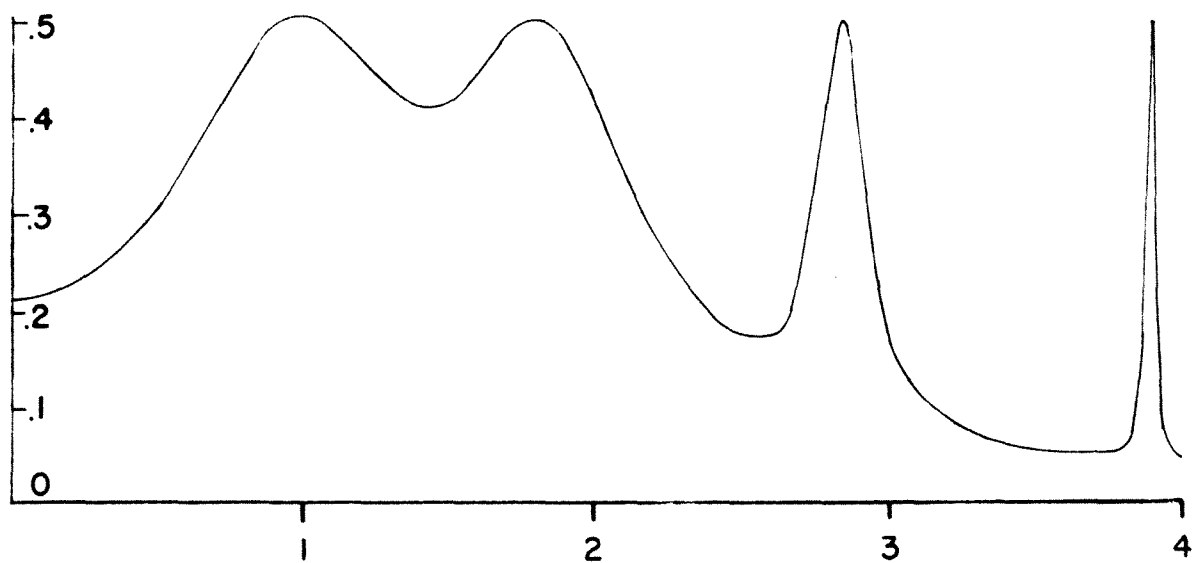


Figure 9b. Average transition probability as a function of y for $w = x = x' = 0.6$, $\delta = 0$.

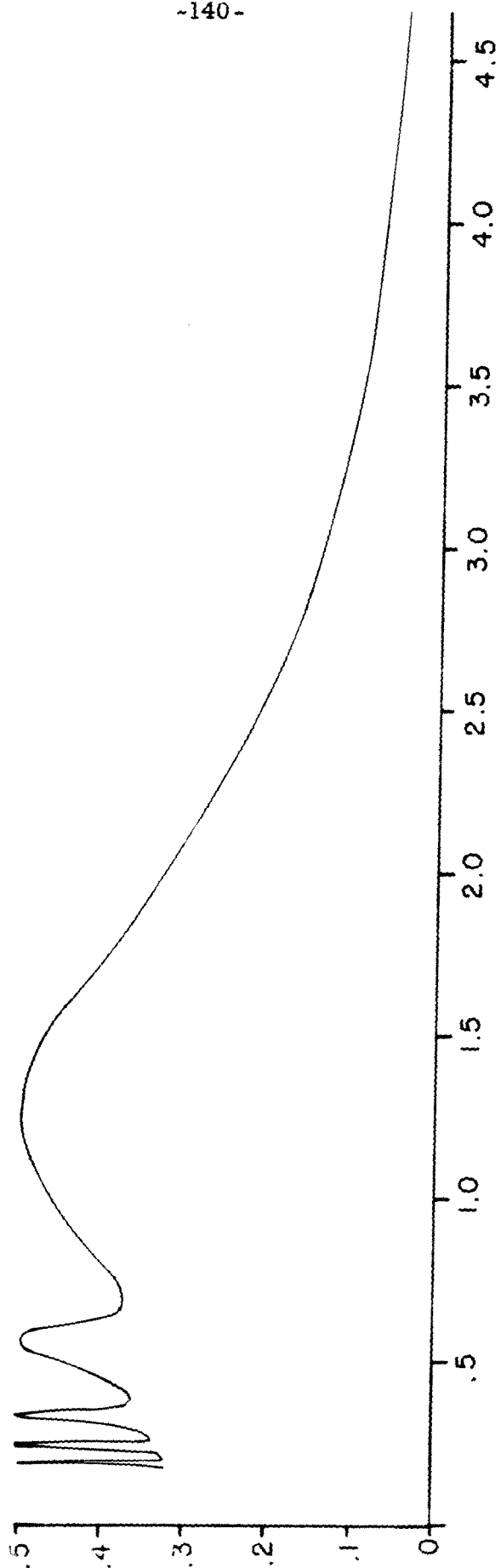


Figure 10. Average transition probability as a function of ω . $\omega_0 = 1$, $c = 1/2$.

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