EXTENDED RATE EQUATIONS*

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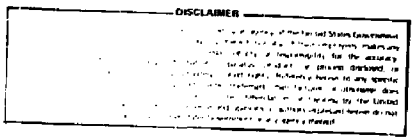
ABSTRACT

I discuss the equations of motion which describe time dependent population flows in an N-level system, reviewing the relationship betwee incoherent (rate) equations, coherent (Schrodinger) equations, and more general partially coherent (Bloch) equations. We discuss approximations which replace the elaborate Bloch equations by simpler rate equations whose coefficients incorporate long-time corsequences of coherence.



INTRODUCTION

We are concerned with the behavior of individual atoms (or molecules) irradiated by laser light. Although any real atom can exist in any of a very large number of discrete internal-energy states, few of the Bohr frequencies $(E_n - E_m)/\hbar$ obtained from energy-level differences will be approximately resonant with a laser frequency. Only states which are connected with the initially populated (ground) state through a succession of near-resonant transitions will receive appreciable excitation from the laser. Thus the description of laser excitation typically proceeds via some truncated set of N basis states representing an N-level atom. Our problem is to find, for specified excitation conditions, the probability $P_n(t)$ that such an N-level system will be found in energy level n at time t, given some initial distribution of probabilities $P_m(0)$ at time t=0.

For a system maintained in thermodynamic equilibrium (TE), at temperature T, the energy-level populations are independent of time and depend only upon the ratio of internal energy E_n to thermal energy kT through the Boltzmann equation

$$P_n^T(t) = g_n \exp [- E_n/kT]/Z$$

Here g_n is the statistical weight of level n and the normalizing factor is the partition function

$$Z = \sum_n g_n \exp [-E_n/kT]$$

The conditions needed for thermodynamic equilibrium are far too stringent for application to laser excitation. (One requires essentially a completely

enclosed hohlraum from which there is negligible escape of vapor or radiation.) One must instead proceed by finding equations which govern the time evolution of level probabilities; the solution of these equations yields the desired populations. Given sufficient time duration, each population will generally reach some constant steady-state value $P_n(\infty)$ which differs from the value $P_n^T(\infty)$ obtained in complete thermodynamic equilibrium. (An exception: purely coherent excitation; populations then continue oscillations indefinitely, although time averages do approach limiting values.)

In the following sections we shall discuss various equations governing the evolution of N-level populations and will comment upon techniques commonly used to solve these.

Throughout our discussion we assume that we begin with an N-level atom in a quiescent state, in the absence of laser irratiation. At time t=0 the atom becomes immersed in the laser field; we require the probabilities $P_n(t)$ at subsequent times, given their initial values $P_n(0)$.

THE RATE EQUATION

The most elementary dynamical equations for populations, long used in astrophysical descriptions of non-equilibrium gases, rests on the assumption that the growth of population in any level n due to another level m is directly proportional to the instantaneous population in level m. That is, we have the rate equation (or master equation)

$$\dot{P}_n(t) = \sum_{m=1}^{N} R_{nm} P_m(t) \qquad n = 1,N$$

expressing a linear relationship between the instantaneous rate of change

$\dot{P}_n(t) \equiv dP_n(t)/dt$ and the instantaneous populations. Here R is a time-independent matrix of rate coefficients: R_{nm} is the rate at which a system known to be in level m undergoes a transition to level n; the diagonal element R_{nn} is the negative of γ_{nn}, the total rate of loss from level n. For a conservative (lossless) N-level system, γ_{nn} is the sum of the transition rates to other discrete levels. More generally, we must include the possibility of ionization or chemical reactions which act as an irreversible drain, at rate r_n, from level n. Thus we have the relationship

$$-R_{nn} \equiv \gamma_{nn} = \sum_{m\neq n=1}^{N} R_{mn} + r_n$$

The individual rate coefficients R_{nm} incorporate both collisional and weak-field radiative effects; one conventionally expresses the latter in terms of the spontaneous emission coefficient (the Einstein A) and a stimulated emission rate proportional to radiation intensity I (and to the Milne B coefficient). Thus R_{nm} can be decomposed in the form

$$R_{nm} = C_{nm} + IB_{mn} + \begin{cases} A_{mn} & \text{if } m>n \\ 0 & \text{if } m\leq n \end{cases}$$

(Note the reversed indices on A and B to conform with convertion.)

It often proves useful to regard the probabilities $P_n(t)$ as the components of an N-dimensional vector. Expressed in operator form, the rate equation reads simply

$$\dot{P}(t) = RP(t)$$

with P(o) given.

Although we have assumed the rate coefficients to be time independent, one can readily treat the situation in which the matrix R changes slowly according to some prescribed (known) formula. We need only divide the time duration into a contiguous succession of subintervals during each of which R remains constant. We then have the succession of initial-value problems

$$\dot{P}(t) = R(1)\, P(t) \qquad o<t<t_1 \quad \text{from } P(o)$$

$$\dot{P}(t) = R(2)\, P(t) \qquad t_1<t<t_2 \quad \text{from } P(t_1)$$

$$\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array}$$

to solve successively for $P(t_1)$, $P(t_2)$, up to $P(t)$.

With passing time the rate-equation solutions approach an asymptotic limit $P(\infty)$. These values, found by setting $\dot{P}(t) = 0$, are solutions to the equations

$$0 = RP(\infty) \equiv \sum_m R_{nm}\, P_m(\infty)$$

That is, $P(\infty)$ is a right eigenvector (null eigenvalue) of the rate-equation operator R.

The presence of coherent sources of light, such as a laser, may invalidate the assumptions which underly the definition of A and B coefficients. Indeed, populations of a laser-irradiated atom undergo well-known (Rabi) oscillations which cannot be obtained as solutions to rate equations. Nevertheless, we shall see that it is possible to obtain modified rate coefficients which can adequately describe appropriate time-averaged population changes or the limiting long-time behavior of populations.

Furthermore, these modified rate coefficients provide a clear distinction between real and virtual energy levels--that is, between processes which proceed by a succession of independent single-photon transitions (whose cumulative effect is multiple-photon excitation), as contrasted with processes which effectively bypass intermediate levels through coherent absorption or emission of several photons (a multi-photon transition).

THE SCHRÖDINGER EQUATION

At the opposite extreme from rate equations, which govern excitation by incoherent processes, one deals with purely coherent excitation wherein phase relationships strongly affect dynamics. In this limit one must obtain the real non-negative probabilities $P_n(t)$ from complex-valued probability amplitudes $C_n(t)$:

$$P_n(t) = |C_n(t)|^2$$

The probability amplitudes $C_n(t)$ are expansion coefficients of the atomic state vector $\psi(t)$ in a basis of atomic energy states ϕ_n:

$$\psi(t) = \sum_{n=1}^{N} C_n(t)\ \phi_n \exp\ [i\phi_n t]$$

The phases ϕ_n appearing in this definition of $C_n(t)$ are completely arbitrary (and may, indeed, be specified as functions of time): one chooses them for convenience in treating the algebra. A common choice, the Schrödinger picture, sets all phases to zero; the Dirac (interaction) picture equates them to Bohr frequencies; the Autler-Townes (rotating-wave) picture obtains phases from the photon frequencies. The rotating-wave picture is particularly suited to treatment of excitation by one

or more nearly sinusoidal driving forces whose frequencies nearly coincide with Bohr frequencies. One can introduce a Rotating Wave Approximation (RWA) to eliminate time variations over intervals comparable to the optical (or Bohr) frequencies. One thereupon obtains the RWA Schrodinger equation

$$i\,\dot{C}_n(t) = \sum_{m=1}^{N} W_{nm}\, C_m(t)$$

where W comprises the matrix elements of the (time-independent) RWA Hamiltonian:

$$W_{nm} = \Delta_{nn} \qquad \text{if } n = m$$
$$= \tfrac{1}{2}\Omega_{nm} \qquad \text{if } n \neq m$$

where Δ_{nn} is the cumulative laser detuning after n steps, and Ω_{nm}, the Rabi frequency, expresses the atom-field interaction which links levels n and m; it is proportional to projection of the atomic dipole-transition moment onto the electric-field vector. Because the basis function phases are arbitrary, one can choose them to make Ω_{nm} real if one wishes.

Like the rate equation, the Schrödinger equation can be written in operator form as a linear equation

$$\dot{C}(t) = -i\,WC(t)$$

As with the rate equation, one can treat slowly varying fields by breaking the time interval into contiguous segments, during each of which the elements of W remain constant.

The RWA Schrödinger equation treats the laser fields as prescribed (classical) time varying fields. That is, it neglects spontaneous emission

compared with stimulated emission. This assumption will be valid if the Rabi periods (ϕ/φ_{mn}) as well as the times of experimental interest are both much shorter than the spontaneous-emission lifetimes.

The RWA approximation assumes also that the sum and difference frequencies $\omega_k \pm \omega_\ell$ of any two lasers are much longer than the characteristic RWA frequencies Δ_{mn} and φ_{mn}. In practice, the frequencies differ by several orders of magnitude, so that the RWA is quite satisfactory.

THE NON-HERMITIAN HAMILTONIAN

Any complete description of an isolated atom must include an infinite set of bound states as well as ionized (continuum) states. When the atom is embedded in a vapor, the complete basis must include a continuum of states which describe the multitude of neighboring (thermal bath) particles. The presence of fields, weak and strong, adds further degrees of freedom. From this milieu we extract an N-level model. If the N-level system were, in fact, a complete closed system, then the total probability would remain unity for all time. This condition translates to the expression

$$\frac{d}{dt}|\psi(t)|^2 = \frac{d}{dt}\sum_{n=1}^{N} P_n(t) = \sum_n \left[\dot{C}_n(t)C_n(t)^* + C_n(t)\dot{C}_n(t)^*\right]$$

$$= -i\sum_{nm}\left\{W_{nm}C_m(t)C_n(t)^* - C_m(t)C_n(t)^* W^*_{mn}\right\}$$

$$= -i\sum_{nm}(W-W^\dagger)_{nm}\, C_m(t)C_n(t)^*$$

Thus an Hermitian Hamiltonian $W = W^\dagger$ assures conservation of probability and, conversely, loss of probability from the N-level subspace can be modelled with a non-Hermitian Hamiltonian. Numerous authors have discussed

the derivation of this effective Hamiltonian, basically by the restriction of a complete Hamiltonian to an N-level subspace. In the simplest approximation the required generalization of W simply adds the decay rates as negative imaginary terms

$$W_{nm} = \Delta_{nm} - i\tfrac{1}{2}\gamma_{nn} \qquad n=m$$

$$= \tfrac{1}{2}\Omega_{nm} \qquad n\neq m$$

THE BLOCH EQUATION

The rate equation and the Schrödinger equation represent two extreme cases of excitation. With rate equations all processes are incoherent: we deal only with excitation probabilities and rate coefficients. The Schrödinger equation, by contrast, treats probability amplitudes; phase relationships between these amplitudes permit interference effects in population changes. These mathematical differences express significant physical differences. With the Schrödinger equation we treat the N-level atom as a closed system, whose basis states permit a complete description. In fact, this N-level system of interest interacts with a larger system, conventionally termed a thermal bath. Although one could, in principle, write a Schrödinger equation for this universe, in practice this would require treating a system with an infinite number of degrees of freedom, whose initial condition we can only specify by probability distributions. Thus the desired equation must eliminate reference to dynamical variables outside the N-level subsystem.

The standard approach to this problem proceeds from the definition of a density matrix $\rho(t)$ as a suitable statistical average over products

of Schrödinger amplitudes $C_n(t)$:

$$\rho_{nm}(t) = \langle C_n(t) C_m(t)^* \rangle = \rho_{mn}(t)^*$$

With this definition the diagonal elements of $\rho(t)$ are the probabilities

$$P_n(t) = \rho_{nn}(t)$$

We require now the equation of motion for $\rho(t)$.

In an incoherent limit, when the interaction between N-level atom and bath is sufficiently strong to destroy any phase relationships between probability amplitudes, we expect to regain rate equations. Expressed in terms of a density matrix $\rho^I(t)$, these read

$$\dot{\rho}^I_{nn}(t) = \sum R_{nm} \rho^I_{mm}(t)$$

At another extreme, we deal with an isolated N-level system whose time evolution is governed by the RWA Hamiltonian W and whose only statistical properties are those associated with probabilistic initial populations. Expressed in terms of the density matrix $\rho^C(t)$ the RWA Schrödinger equation becomes the RWA Liouville equation

$$\dot{\rho}^C_{nm}(t) = -i \sum_k \left[W_{nk} \rho^C_{km}(t) - \rho^C_{nk}(t) W^+_{km} \right]$$

Note that the derivation of the Liouville equation requires that W be independent of the statistical average $\langle \cdots \rangle$. Thus, W cannot express the interaction between the N-level system and the bath; the Liouville equation expresses the same coherent evolution as does the Schrödinger equation, although it permits a concise expression for probabilistic initial conditions.

To interpolate between these two extremes we require an equation valid for any $\rho(t)$. As many authors have shown, we can begin a derivation by recognizing that the system of interest, the N-level atom, is only a small subsystem of a large closed system of atom plus bath. In principle we could describe this closed system with either a Schrödinger equation or, equivalently, a Liouville equation. To label the basis states of this full space one must augment the discrete N-level label ^{n} with supplementary continua, say α, which define the states of the bath. The statistical average $< >$ used in defining the density matrix $\rho(t)$ is then of the form

$$\rho_{nm}(t) = \sum_{\alpha} p_{\alpha} C_{n\alpha}(t)\, C_{m\alpha}(t)^{*}$$

where the Schiff symbol $\sum_{\alpha}$ indicates summation over discrete variables and integration over continuum variables; p_{α} is the probability of observing the bath state labeled by α. This expression for the statistical average, taken with bath states of equal likelihood ($p_{\alpha} = 1$), can be regarded as a summation over those elements of a matrix

$$\hat{\rho}_{n\alpha,m\alpha'}(t) = C_{n\alpha}(t)\, C_{m\alpha'}(t)^{*}$$

which are diagonal in bath labels α. The matrix $\rho_{nm}^{(t)}$ obtained by this trace procedure is therefore often termed a <u>reduced density matrix</u>: it refers to only a finite part of a larger closed system.

Because the full atom-bath Hamiltonian incorporates the interaction between atom and bath, the trace procedure does not immediately yield an equation for $\rho(t)$. One must, by approximation, neglect terms which are

off-diagonal in bath labels. The resulting Bloch equation (also known as the transport equation or the Boltzmann equation) can be written

$$\dot{\rho}_{nm}(t) = -i \sum_k \left[W_{nk}\, \rho_{km}(t) - W^*_{mk}\, \rho_{nk}(t) \right] + \begin{cases} \sum_{k \neq n} R_{nk}\, \rho_{kk}(t) & \text{if } n=m \\ -\left(\frac{1}{T_2}\right)_{nm} \rho_{nm}(t) & \text{if } n \neq m \end{cases}$$

That is, the Bloch equation combines the action of the Liouville operator expressing coherent dynamics with the rate equation operator expressing incoherent population changes; the final term expresses possible relaxation of off-diagonal elements of $\rho(t)$ by elastic collisions, in addition to the inelastic-collision relaxation already produced by W.

In writing the Bloch equation in this form we assume that the diagonal elements W_{nn} incorporate the total rate of loss from level n. The restriction $k \neq n$ in the second sum then avoids repetition of the total loss. As an example, when the laser + atom Hamiltonian has matrix elements only between adjacent energy levels, the equation for population $P_2(t) = \rho_{22}(t)$ has the form

$$\dot{\rho}_{22} = -\gamma_{22}\rho_{22} + R_{21}\rho_{11} + R_{23}\rho_{33} + \cdots + \mathrm{Im}\left\{ \Omega_{21}\rho_{12} + \Omega_{23}\rho_{32} \right\}$$

which differs from a rate equation by the presence of the terms involving density-matrix elements ρ_{12} and ρ_{32} from the first super- and sub-diagonal. In turn, elements once removed from the diagonal are related to elements

ρ_{12} and ρ_{32} from the first super- and sub-diagonal. In turn, elements once removed from the diagonal are related to elements still further from the diagonal; for example

$$\dot{\rho}_{23} = -\left[\gamma_{23} + i\Delta_{23}\right]\rho_{23} - \tfrac{1}{2}\Omega_{23}(\rho_{33} - \rho_{22}) + \tfrac{1}{2}\left\{\Omega_{21}\rho_{13} - \Omega_{43}^{*}\rho_{24}\right\}$$

and, in turn,

$$\dot{\rho}_{24} = -\left[\gamma_{24} + i\Delta_{24}\right]\rho_{24} + \tfrac{1}{2}\left\{\Omega_{21}\rho_{14} + \Omega_{23}\rho_{34} - \Omega_{34}^{*}\rho_{23} - \Omega_{54}^{*}\rho_{25}\right\}$$

Like the Schrödinger and rate equations, the Bloch equation is a linear equation with constant coefficients: it has the form

$$\dot{\rho}_{nm}(t) = \sum_{n'm'} M_{nm,n'm'}\rho_{n'm'}(t)$$

where the non-zero elements of M are

$$M_{nn,nn} = -\gamma_{nn} \equiv \sum_{k\neq n} R_{kn} + r_n$$

and, for $m\neq n$

$$M_{mm,nn} = R_{mn}$$

$$M_{mn,mn} = \gamma_{mn} + i\Delta_{mn}$$

and, for any m,n

$$M_{mn,\,kn} = \frac{i}{2}\,\Omega_{mk}$$

$$M_{nm,\,nk} = -\frac{i}{2}\,\Omega^{+}_{km} = -\frac{i}{2}\,\Omega_{mk}$$

Here, r_n is the ionizing (i.e., probability non-conserving) loss rate from level n and R_{mn} is the collisional (and/or spontaneous emission rate) for transition n→m. The sum of all these inelastic collisional loss terms is often denoted by $(1/T_1)$,

$$\left(\frac{1}{T_1}\right)_n \equiv \sum_{k\neq n} R_{kn}$$

so that the relaxation rate of the diagonal element $\rho_{nn}(t)$, given by $-M_{nn,nn}$, is expressible as

$$\gamma_{nn} = \left(\frac{1}{T_1}\right)_n + r_n$$

The real numbers Δ_{mn} express cumulative detuning of the lasers which link levels m and n. The real numbers γ_{mn} which express the damping rate of element $\rho_{mn}(t)$ are often denoted $\left(\frac{1}{T_2}\right)_{mn}$. They obtain from the population loss rates γ_{mm} and γ_{nn} for the levels m and n upon addition of the relaxation term $(1/T_2')$:

$$\gamma_{mn} \equiv \left(\frac{1}{T_2}\right)_{mn}$$

$$= \frac{1}{2}(\gamma_{mm} + \gamma_{nn}) + \left(\frac{1}{T_2'}\right)_{mn}$$

Recalling the definition of $(1/T_1)_n$ we can write

$$\left(\frac{1}{T_2}\right)_{mn} = \frac{1}{2}\left(\frac{1}{T_1}\right)_m + \left(\frac{1}{T_1}\right)_n + r_m + r_n + \left(\frac{1}{T_2}'\right)_{mn}$$

That is, the relaxation of the off-diagonal element $\rho_{mn}(t)$, given by $-M_{mn,mn} \equiv \left(\frac{1}{T_2}\right)_{mn}$ occurs because of inelastic collisional loss and ionization loss from levels m and n and, in addition, because of elastic (phase changing) collisions. Evidently one has the inequality

$$\left(\frac{1}{T_2}\right)_{mn} \geq \frac{1}{2}\left[\left(\frac{1}{T_1}\right)_m + \left(\frac{1}{T_1}\right)_n\right]$$

with equality prevailing in the absence of ionization or elastic collisions.

Although the Bloch equation introduces an array M whose elements are identified by four indices, such labeling is merely a convenient convention. One can, alternatively, serialize the N^2 elements of ρ in any convenient ordering identified by a single running index. For example, the new index

$$I = (n-1)\,N + m$$

which runs from 1 to N^2 provides one such scheme. We thereby organize the elements of M into a two-dimensional array. The Bloch equation then takes the form of a vector equation

$$\dot{\rho}_I(t) = \sum_J M_{IJ}\,\rho_J(t)$$

or, simply, as the operator equation

$$\dot{\rho}(t) = M\rho(t).$$

For example, consider a two-level atom for which ionization occurs only from level 2 at a rate r. Then if we order the matrix elements of ρ as $[\rho_{11}, \rho_{22}, \rho_{12}, \rho_{22}]$ we have for M the 4x4 matrix

$$\begin{bmatrix} 0 & \left(\frac{1}{T_1}\right) & \frac{i\Omega}{2} & -\frac{i\Omega}{2} \\ 0 & -\left[\left(\frac{1}{T_1}\right) + r\right] & -\frac{i\Omega}{2} & +\frac{i\Omega}{2} \\ \frac{i\Omega}{2} & -\frac{i\Omega}{2} & -i\Delta - \left\{\frac{1}{2}\left[\frac{1}{T_1} + r\right] + \frac{1}{T_2'}\right\} & 0 \\ -\frac{i\Omega}{2} & +\frac{i\Omega}{2} & 0 & i\Delta - \left\{\frac{1}{2}\left[\frac{1}{T_1} + r\right] + \frac{1}{T_2'}\right\} \end{bmatrix}$$

We have here used $\left(\frac{1}{T_1}\right)$ as the (collisional) de-excitation rate for $2 \to 1$, and have neglected the rate $1 \to 2$, as is appropriate for a de-excitation by a cold bath. We have expressed the phase relaxation rate as $\left(\frac{1}{T_2}\right)$.

For future reference we note that, because γ_{nm} is the sum of all collisional transitions leading out of level n, elements of M satisfy the summation property

$$\sum_m M_{mm,nn} = r_n$$

Furthermore the following summation property holds

$$\sum_m M_{mm,k\ell} = M_{\ell\ell,k\ell} + M_{kk,k\ell}$$

$$= \frac{i}{2}\left(\Omega_{\ell k} - \Omega^*_{k\ell}\right) = 0$$

EXACT SOLUTIONS: EXPONENTIAL FORMS

All of the foregoing dynamical equations are linear equations with constant coefficients. For such equations one can employ well-known standard methods to obtain solutions. The simplest expression obtains after rewriting the equation in operator form,

$$\dot{\rho}(t) = M\,\rho(t)$$

as the formal solution

$$\rho(t) = e^{Mt}\,\rho(o)$$

This expression is only formal, because it requires evaluation of the exponential of the operator (super-matrix) M. Perhaps the simplest evaluation of this exponential proceeds through the definition of the exponential as a power series

$$e^{Mt} = 1 + Mt + M^2\,\frac{t^2}{2!} - \ldots$$

This formula, truncated after N terms, provides a satisfactory algorithm for integrating the linear equation over a finite N-dependent time interval. Other power-series expressions are also possible, such as

$$e^{Mt} = \left[e^{-Mt/2}\right]^{-1} e^{Mt/2}$$

$$= \left[1 - M\left(\frac{t}{2}\right) + \frac{M^2}{2!}\left(\frac{t}{2}\right)^2 + \ldots\right]^{-1}\left[1 + M\left(\frac{t}{2}\right) + \frac{M^2}{2!}\left(\frac{t}{2}\right)^2 - \ldots\right]$$

which permit longer time intervals for a given N-term expansion of the exponential.

Note that once we have a procedure for evaluating the time evolution with a constant operator M, we can readily treat problems in which M changes slowly: we replace the slowly varying functions by step functions, so that the time evolution is described by a succession of constant operators M(1), M(2), ... We then have

$$\rho(t) = e^{M(1)t}\,\rho(o) \qquad t_1 \geq t \geq o$$

$$= e^{M(2)(t-t_1)}\,\rho(t_1) \qquad t_2 \geq t > t_1$$

$$= e^{M(3)(t-t_2)}\,\rho(t_2) \qquad t_3 \geq t > t_2$$

$$= \text{etc.}$$

That is, the final density matrix obtains after a succession of exponential operators act:

$$\rho(\infty) = \ldots e^{M(3)(t_3-t_2)}\, e^{M(2)(t_2-t_1)}\, e^{M(1)t_1}\,\rho(o)$$

$$\equiv e^{\bar{M}}\,\rho(o)$$

Note that because the operators M(k) do not commute we cannot employ the operator

$$\exp\left[\int_o^t dt\, M(t)\right]$$

to evaluate the time dependence. One can, for example, construct time dependence for which the time integral $\int dt\, M(t)$ is the null matrix but to which, nevertheless $\bar{M}$ is not the null matrix.

EIGENVECTOR METHOD

Power-series integration techniques are well suited to modest time intervals; they require only repeated matrix multiplication. However, for the study of very long (in the limit, infinite) time intervals, an alternative approach is widely used: we introduce right eigenvectors (bras) $|\lambda\rangle$ and left eigenvectors (kets) $\langle\lambda|$ of the Bloch operator M

$$M|\lambda\rangle = \lambda|\lambda \qquad\qquad \langle\lambda|M = \lambda\langle\lambda|$$

and use these complete states to express the exponential:

$$\rho(t) = \sum_{\lambda} |\lambda\rangle\, e^{\lambda t}\, \langle t|\, \rho(o)$$

That is, we have the formula

$$\rho_{mn}(t) = \sum_{\lambda} e^{\lambda t} \sum_{m'n'} \langle mn\,|\lambda\rangle\, \langle\lambda|m'n'\rangle\, \rho_{m'n'}(o)$$

where $\langle mn|\lambda\rangle$ and $\langle\lambda|m'n'\rangle$ are obtained as solutions to be the eigenvalue equations

$$\sum_{m'n'} M_{mn,m'n'} \langle m'n'|\lambda\rangle = \lambda\, \langle mn|\lambda\rangle$$

$$\sum_{m'n'} M_{m'n',mn}\, \langle\lambda|m'n'\rangle = \lambda\, \langle\lambda|mn\rangle$$

Prior to the turn-on of laser irradiation at time $t = o$ there is no coherence. Thus the initial condition is that the density matrix be diagonal

$$\rho_{mn}(o) = \delta_{mn}\, P_n(o)$$

One thus has for the diagonal elements the formula

$$P_n(t) = \sum_\lambda e^{\lambda t} \sum_m \langle nn|\lambda\rangle \langle\lambda|mm\rangle P_m(0)$$

We see that the density matrix can be expressed as a sum of eigensolutions, or Fourier components,

$$\rho(t) = \sum_\lambda \rho^\lambda(t) = \sum_\lambda e^{\lambda t} \rho^\lambda$$

where the elements of $\rho^\lambda(t)$ are constructed according to the prescription

$$\rho^\lambda_{nn}(t) = \sum_{m'n'} e^{\lambda t} \langle nn|\lambda\rangle \langle\lambda|m'm'\rangle P_{m'}(0)$$

That is, the eigensolution $\rho^\lambda(t)$ decays at the rate λ

$$\dot{\rho}^\lambda(t) = \lambda \rho^\lambda(t)$$

where λ is an eigenvalue of M. The steady-state solutions (those which do not change with time) are evidently the elements ρ°_{nm} corresponding to zero eigenvalue. For probabilities the Fourier expansion is

$$P_n(t) = \sum_\lambda P^\lambda_n(t)$$

The eigenvalues λ are, in general, complex. The real parts are the negative of characteristic decay rates, the imaginary parts provide characteristic population oscillation frequencies. After a sufficiently long time, only those eigensolutions with null eigenvalues, $\lambda_0 = 0$, will

contribute to the solution. One can thus obtain the limiting infinite-time populations from only the zero-eigenvalue eigenvector:

$$P_n(\infty) = P_n^o$$

$$= \sum_{\lambda_o} \sum_{m} \langle nn|\lambda_o\rangle \langle \lambda_o|mm\rangle P_m(o)$$

Although the construction of $P_n(t)$ makes use of only a subset of eigenvector components (those $\langle mn|\lambda\rangle$ for which $m = n$) the entire set are of course required for normalization:

$$1 = \langle\lambda|\lambda\rangle = \sum_{n} \langle\lambda|nn\rangle \langle nn|\lambda\rangle + \sum_{m\neq n} \langle\lambda|mn\rangle \langle mn|\lambda\rangle$$

As we shall see, the null eigenvalue λ_o provides an exception when there is no ionization; the components $\langle\lambda_o|mn\rangle$ with $m\neq n$ are then zero.

The preceding discussion can be summarized as follows:

1) First construct the matrix of coefficients M (of size $N^2 \times N^2$ for an N-level atom)
2) Find the eigenvalues λ (N complex numbers)
3) Find the (normalized) eigenvector components $\langle nn|\lambda\rangle$ and $\langle\lambda|mn\rangle$ (all N^2 components of $\langle mn|\lambda\rangle$ are needed for normalization)
4) Using N components $\langle nn|\lambda\rangle$ of each eigenvector, construct the solution.

PARTITIONING METHODS

The foregoing procedure deals with the full density matrix $\rho_{nm}(t)$ of N^2 elements; one obtains solutions by finding the N^2 eigenvalues and (normalized) eigenvectors of the $N^2 \times N^2$ matrix M. Because one ultimately deals only with the N diagonal elements $\rho_{nn}(t)$ it is useful to obtain equations which deal only with these quantities.

Following the lead of Løwdin, Feshbach, Mower, Zwanzig, and others, we partition the full density matrix ρ into a diagonal part P and the remainder Q:

$$\rho_{nm}(t) = \begin{cases} P_n(t) & n = m \\ Q_{nm}(t) & n \neq m \end{cases}$$

We similarly partition M:

$$\rho = \begin{bmatrix} P \\ Q \end{bmatrix} \qquad M = \begin{bmatrix} R & iU \\ iV & B \end{bmatrix}$$

Then the Bloch equation takes the form

$$\boxed{\begin{aligned} \dot{P}(t) &= R\,P(t) + i\,U\,Q(t) \\ \dot{Q}(t) &= +iV\,P(t) + B\,Q(t) \end{aligned}}$$

Here R is the matrix of rate-equation coefficients which apply in the absence of laser excitation, U and V are matrices of Rabi frequencies, and B combines relaxation rates and Rabi frequencies.

For example, the previously considered two-level atom has matrices

$$R = \begin{bmatrix} 0 & \left(\frac{1}{T_1}\right) \\ 0 & -\left(\frac{1}{T_1} + r\right) \end{bmatrix}$$

$$U = V = \frac{\Omega}{2}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

$$B = \begin{bmatrix} -i\Delta - \gamma & 0 \\ 0 & i\Delta - \gamma \end{bmatrix} \quad \text{where} \quad \gamma = \frac{1}{2}\left[\frac{1}{T_1} + r\right] + \left(\frac{1}{T_2'}\right)$$

Let us now look at the (exact) solution to these equations in terms of eigenvectors.

PARTITIONED EIGENVECTORS

The eigenket equation

$$[W - \lambda\, 1]\,|\lambda\rangle = 0$$

when expressed in partitioned form, becomes

$$\begin{bmatrix} R-\lambda & iU \\ iV & B \end{bmatrix}\begin{bmatrix} |P\lambda\rangle \\ |Q\lambda\rangle \end{bmatrix} = 0$$

where $|P\lambda\rangle$ has only components of the (diagonal) form $\langle nn|\lambda\rangle$ and $|Q\lambda\rangle$ comprises the remaining components $\langle nm|\lambda\rangle$ with $m \neq n$. That is, we have the coupled equations

$$(R-\lambda)|P\lambda\rangle + i\,U\,|Q\lambda\rangle = 0$$

$$iV\,|P\lambda\rangle + (B-\lambda)|Q\lambda\rangle = 0$$

To obtain an equation involving only $|P\lambda\rangle$ we solve the second of these equations for $|Q\lambda\rangle$ in terms of $|P\lambda\rangle$ and substitute this expression back into the first equation, thereby obtaining the eigenvalue equation in the

non-linear form

$$\boxed{\left[R + U\,\frac{1}{B-\lambda}\,V - \lambda 1\right]\,|P\lambda\rangle = 0}$$

That is, the eigenvectors $\langle nn|P\lambda\rangle = \langle nn|\lambda\rangle$ needed for the construction of $P_n(t)$ are solutions to the non-linear eigenvalue equation

$$\sum_m \left[R + U\,\frac{\lambda}{B-\lambda}\,V\right]_{nm} \langle mm|P\lambda\rangle = \lambda\ \langle nn|P\lambda\rangle$$

Using these eigenvectors we construct the separate Fourier components

$$P_n^\lambda(t) = e^{\lambda t} \sum_m \langle nn|P\lambda\rangle\ \langle P\lambda|mm\rangle\ P_m(o)$$

which in turn contribute to the total probability

$$\boxed{P_n(t) = \sum_\lambda P_n^\lambda(t) = \sum_\lambda e^{\lambda t} P_n^\lambda}$$

Each of these Fourier components satisfies the non-linear eigenvalue equation

$$\boxed{\lambda P^\lambda(t) = \left[R + U\,\frac{1}{B-\lambda}\,V\right]\ P^\lambda(t) = R^E(\lambda)\ P^\lambda(t)}$$

Here the effective eigenvalue-dependent rate-equation matrix is

$$R^E(\lambda) = R + U\,\frac{1}{B-\lambda}\,V$$

As can readily be appreciated, the partitioning technique introduces, without approximation, a non-linear eigenvalue equation for $P^{\lambda}(t)$ in place of the linear-eigenvalue problem of the Bloch equation,

$$\left[M - \lambda \right] \rho^{\lambda}(t) = 0$$

The partitioning technique, in which one eliminates explicit reference to a portion of a complete space (usually an infinite subspace) in order to deal with a few-dimensional subspace has been used extensively to justify the use of an effective energy-dependent non-Hermitian Hamiltonian--the so-called optical potential of nuclear reaction theory. Here we find, by analogy, the appearance of eigenvalue-dependent effective rate coefficients, $R^{E}(\lambda)$.

These rate coefficients only have meaning when applied to the appropriate Fourier component. That is, using the fact that the time dependence of $P^{\lambda}(t)$ is, by definition, $e^{\lambda t}$, we have

$$\dot{P}^{\lambda}(t) = \lambda P^{\lambda}(t)$$

or, using the eigenvalue equation, we have

$$\dot{P}^{\lambda}(t) = R^{E}(\lambda) P^{\lambda}(t) = \left[R + U \frac{1}{\beta - \lambda} V \right] P^{\lambda}(t)$$

The rate equation appearance of this equation (termed the Generalized Master Equation or GME by Goodman and Stone) disguises its true nature as an eigenvalue equation: we know a priori that the time dependence is simply $e^{\lambda t}$ and that the operator $R^{E}(\lambda)$ can be replaced by the number λ. Thus it does not actually represent an equation governing time dependence.

The time dependence of P(t), rather than the component $P^{\lambda}(t)$, is governed by the equation

$$\dot{P}(t) = \sum_{\lambda} R^{E}(\lambda)\, P^{\lambda}(t)$$

$$= R\, P(t) + \sum_{\lambda} U \frac{1}{B-\lambda} V\, P^{\lambda}(t)$$

which does not provide an equation involving P(t) alone.

The non-linear dependence upon λ incorporates all of the effects of coherence which the Bloch equation admits. Thus the eigenvalues and eigenvectors remain unchanged by the reformulation. Indeed, the original Bloch equation is more straightforward to solve. The non-linear form, though perhaps obscuring the functional behavior of λ, invites solution by iteration through a succession of more refined approximations to λ, say starting from λ=0 or from the eigenvalues of R. One possible advantage of the more complicated equation arises from the possibility of truncating the iteration, thereby obtaining an approximation $\bar{R}^{E} \equiv R^{E}(\bar{\lambda})$. It may also happen that symmetries of the Bloch operator M make the partitioned technique particularly simple to apply, once the eigenvalues are known.

TRANSFORM SOLUTIONS

Linear equations lend themselves to solution by Laplace transform. If we denote by $\tilde{\rho}(s)$ the transform of $\rho(t)$,

$$\tilde{\rho}_{mn}(s) = \int_{0}^{b} dt\, e^{-st}\, \rho_{mn}(t)$$

$$\rho_{mn}(t) = \int_{c} ds\, e^{st}\, \tilde{\rho}_{mn}(s)$$

then the Bloch equation, in transform space, becomes

$$s\tilde{\rho}(s) - \rho(o) = M\,\tilde{\rho}(s)$$

From the formal solution to this equation, involving the resolvent operator $(s - m)^{-1}$

$$\tilde{\rho}(s) = \frac{1}{s-m}\ \rho(o)$$

we obtain the formal expression for $\rho(t)$:

$$\boxed{\rho(t) = \int_C ds\ e^{st}\ \frac{1}{s-M}\ \rho(o)}$$

This formula can be recognized as a contour integral representation of the exponential time evolution operator. Alternatively, we can introduce the eigenvector expansion of M to recover our preceding expressions.

In partitioned form, the transform method yields the equations

$$s\tilde{P}(s) - P(o) = R\,\tilde{P}(s) + i\,U\,\tilde{Q}(s)$$

$$s\tilde{Q}(s) = iV\,\tilde{P}(s) + B\,\tilde{Q}(s)$$

or

$$\left[s - R + U\,\frac{1}{s-B}\,V\right]\,\tilde{P}(s) = P(o)$$

with the solution

$$P(t) = \int_C ds\ e^{st}\,\frac{1}{s - R - U\,\frac{1}{B-s}\,V}\ p(o)$$

Again we can proceed by finding eigenvectors; we recover the previous expressions for P(t).

TIME INTEGRATION

The eigenvalue approach just described amounts to solution by Laplace transform. An alternative formulation proceeds by formal solution of the time-dependent equation for Q(t):

$$Q(t) = i \int_0^t ds\, e^{+Bs}\, V\, P\,(t-s)$$

(where we use the property $Q(o) = o$).

This yields for P(t) the coupled integro-differential equation

$$\dot{P}(t) = R\,P(t) - \int_0^t ds\, Ue^{Bs}\, V\, P(t-s)$$

Kenkre has termed such an equation the Generalized Master Equation. Like the previous expressions for P(t), this formula incorporates all of the properties of the Bloch equation. Here the effects of coherence are manifested through the convolution integral which introduces a memory into the equation for instantaneous change.

SOLUTIONS

We have seen that the Bloch equation can be recast into many forms, each of which incorporates all of the effects of coherence and incoherence which the original equation contained. Let us examine some possible approximations to these alternative expressions.

APPROXIMATION I: EIGENVECTOR TRUNCATION

The exact solution to the Bloch equation can be expressed as a Fourier series, with frequencies obtained as eigenvalues of the Bloch operator M. An obvious approximation procedure truncates this expansion of $\rho(t)$ after a few terms. We then have solutions of the form

$$\rho(t) = \rho^{o} + \rho^{\lambda_1}(t) + \ldots.$$

where each successive term is constructed from eigenvectors and eigenvalues of M. The first term, ρ^{o} corresponding to eigenvalue $\lambda_o = 0$, yields the asymptotic $t \to \infty$ populations.

Although the exact solution requires all Fourier components, the high frequency components contribute only to the transient behavior and to population oscillations about slowly varying means. Thus a few terms of this expansion should be adequate to express the general behavior of $\rho(t)$.

APPROXIMATION II: PARTITIONING

The eigenvalue equation for the Fourier components $P^{\lambda}(t)$,

$$\left[R^{E}(\lambda)-\lambda\right] P^{\lambda}(t) \equiv \left[R + U \frac{1}{B-\lambda} V - \lambda\right] P^{\lambda}(t) = 0$$

involves λ non-linearly. If the effects of coherence are small, then R dominates the operator $U\,(B-\lambda)^{-1}\,V$, and one can approximate the eigenvalues of $R^{E}(\lambda)$ with those of R:

$$\left[R - \mu\right] C^{\mu} = 0$$

Taking each μ in turn, one solves the linear eigenvalue problem

$$\left[R^E(\mu) - \lambda\right] C^\lambda(\mu) \equiv \left[R + U \frac{1}{B-\mu} V - \lambda\right] C^\lambda(\mu) = 0$$

Each μ yields a new set of eigenvalues λ, so that λ is a function of μ, say $\lambda(\mu)$, known at discrete points. The curve intersections $\lambda(\mu) = \mu$ are the Bloch eigenvalues.

APPROXIMATION III: WILCOX-LAMB

An alternative approach assumes that, after a transient period of no interest, the off-diagonal elements of P(t) achieved steady state values commensurate with the instantaneous values of P(t):

$$\dot{Q}(t) \tilde{=} 0$$

The subsequent solution for Q(t) in terms of P(t),

$$Q(t) = - iB^{-1} V P(t)$$

represents adiabatic elimination of the off-diagonal elements. This formula for Q(t), in turn, yields the Wilcox-Lamb (rate) equation

$$\dot{P}^W(t) = \left[R + U \frac{1}{B} V\right] P^W(t)$$
$$\equiv R^W P^W(t)$$

An alternative derivation is to truncate the series

$$\dot{P}(t) = R\,P(t) + \sum_{\lambda} U \frac{1}{B-\lambda} V\, P^{\lambda}(t)$$
$$= R\,P(t) + U \frac{1}{B} V \dot{P} + \ldots .$$

by assuming that time has progressed sufficiently far that the coherent-excitation contribution to $\dot{P}(t)$ differs little from the contribution at $t \to \infty$. We then substitute $P^{0} \tilde{=} P(t)$ on the right-hand side and obtain the WL equation. Thus the WL rate matrix R^{W} is identical with the zero-eigenvalue GME $R^{E}(0)$:

$$R^{W} = R^{E}(0) = R + U \frac{1}{B} V$$

For the elementary two-level atom the WL rate matrix has the structure

$$R^{W} = \begin{bmatrix} 0 & \left(\frac{1}{T_1}\right) \\ 0 & -\left(\frac{1}{T_1} + r\right) \end{bmatrix} + \frac{2\gamma}{\gamma^2 + \Delta^2} \left(\frac{\Omega}{2}\right)^2 \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

where

$$\gamma = \frac{1}{2} \left[\frac{1}{T_1} + r\right] + \left(\frac{1}{T_2'}\right)$$

This equation describes relaxation processes with two time scales: The energy-changing (inelastic collision) processes which alter diagonal elements during a characteristic time termed T_1; and energy-conserving (elastic collision) processes which alter the off-diagonal elements during a time termed T_2'. For more complicated systems the matrix R is the generalization of $1/T_1$, whereas the diagonal elements of B are

generalizations of the sum $(1/T_1) + (1/T_2)$. The validity of the Wilcox-Lamb approximation rests on the assumption that the elastic-scattering relaxation of B occurs more rapidly than does the relaxation from R. When this is not true, the adiabatic elimination of Q(t) is not valid.

APPROXIMATION III: FIRST-ORDER WL

Let us introduce a course-graining in time by averaging over some time interval τ:

$$< F(t) > = \frac{1}{2\tau} \int_{t-\tau}^{t+\tau} ds\, \Gamma(s)$$

Then from the integral form for P(t) we obtain

$$< \dot{P}(t) > = R \quad P(t)$$

$$- \frac{1}{2\tau} \int_{t-\tau}^{t+\tau} dt \int_{0}^{t} as\, U\, e^{Bs}\, V\, P(t-s)$$

We now make three approximations. First, we assume that the course-graining average has no appreciable effect upon the interval size $(t-\tau, t+\tau)$ over which the convolution integral goes. This approximation allows us to write

$$< \dot{P}(t) > = R < P(t) > - \int_{0}^{t} ds\, U\, e^{Bs}\, V < P(t-s) >$$

Next we expand the averaged probability in a Taylor series, retaining only two terms:

$$< P(t-s) > \tilde{=} < P(t) > - s < \dot{P}(t) >$$

Upon doing the integrals we obtain the expression

$$\langle \dot{P}(t) \rangle - R \langle P(t) \rangle - U \left(\frac{e^{Bt} - 1}{B}\right) V \langle P(t) \rangle$$

$$- U \left[\frac{e^{Bt}(Bt+1)}{B^2} - \right] V \langle \dot{P}(t) \rangle$$

Lastly, we look at times sufficiently long that the exponential e^{-Bt} no longer makes an appreciable contribution. That is, we neglect transient phenomena. We thereby obtain the equation

$$\boxed{\dot{P}^F(t) = - \left[1 - U \frac{1}{B^2} V\right]^{-1} \left[r + U \frac{1}{B} V\right] P^F(t) = R^F P^F(t)}$$

wherein we introduce the notation $P^F(t)$ for $\langle P(t) \rangle$.

APPROXIMATION IV: HIGHER-ORDER WL

One can, of course, include higher terms in the Taylor series for $< P(t-s) >$. This is most readily done if we first take the limit of $t \to \infty$ in the time integral. This limit expresses our neglect of transient phenomena:

$$< \dot{P}(t) > = R < P(t) > - \int_0^\infty ds\, U\, e^{\beta s}\, V < P(t-s) >$$

We now write, in operator form,

$$< P(t-s) > = \exp\left[-s \frac{d}{dt}\right] < P(t) >$$

When integrated over s the equation then becomes

$$\dot{P}(t) + R < P(t) > - U \frac{1}{B - \frac{d}{dt}} \cdot V < P(t) >$$

or, on expanding the operator fraction and dropping the bracket notation

$$\dot{P}(t) = R\, P(t) - U \frac{1}{B} V\, P(t) + U \frac{1}{B^2} V \dot{P}(t)$$

$$- U \frac{1}{B^3} V \ddot{P}(t) + \ldots$$

We can truncate this equation with some derivative, say $\ddot{P}(t)$, which we in turn obtain by differentiating $\dot{P}(t)$. This procedure will yield increasingly complicated expressions involving $P(t)$ and $\dot{P}(t)$ which can be cast into rate-equation form.

Alternatively, one can clear the equation of operator fractions by multiplying by $U(B + \frac{d}{dt}) U^{-1}$. The result is

$$\ddot{P}(t) + (\tilde{B} + R)\,\dot{P}(t) + (\tilde{B}R + UV)\,P(t) = 0$$

where

$$\tilde{B} = U\,B\,U^{-1}$$

Rewritten as a psuedo rate equation, this reads

$$\dot{P}(t) = \frac{1}{\tilde{B}+R}\,(\tilde{B}R + UV)\,P(t) - \frac{1}{\tilde{B}+R}\,\ddot{P}(t)$$

PROPERTIES OF APPROXIMATE SOLUTIONS

We have seen the Bloch equation has, as exact solutions, the eigenvalue expansion

$$P(t) = \sum_{\lambda} e^{\lambda t} P^{\lambda}$$

where the components P^{λ} are to be constructed from selected elements of left and right eigenvectors of the Bloch operator M:

$$P_n^{\lambda} = \sum_{m} < nn|\lambda > < \lambda|mm > P_m(0)$$

where

$$< \lambda|M = \lambda < \lambda| \quad \text{and} \quad M|\lambda > = \lambda|\lambda >$$

Although we here only need the elements $< nn|\lambda >$ with $n=m$, in general all of the eigenvector components are required to construct the normalization:

$$1 = < \lambda|\lambda > = \sum_{m} \Big\{ < \lambda|mm > < mm|\lambda > + \sum_{n \neq m} < \lambda|nm > < nm|\lambda > \Big\}$$

An exception occurs for the null eigenvalue, $\lambda = 0$. We rewrite the previously noted property

$$\sum_{nm} M_{rm,k} = \delta_{k,0} r_p$$

in operator form as

$$< 1_p|M = < 1_p|r$$

where $< 1_p|$ is the bra whose components are

$$< 1_p|mn > = 1 \quad \text{if } m=n$$

$$= 0 \quad \text{if } m \neq n$$

and r is a diagonal matrix with elements r_n. Thus if there are no probability losses, $r_n = 0$, the bra $< 1_p|$ provides, by simple construction, a left eigenvector of M with zero eigenvalue. For this case we require only the diagonal elements of the right eigenvectors in order to normalize the eigenvector:

$$1 = < \lambda_o|\lambda_o > = \sum_m < 1_p^*|mm > \; < mm|\lambda_o >$$

$$= \sum_m < mm|\lambda_o >$$

Our various master-equation approximations to the Bloch equation are, like the original equation, amenable to solution by eigenvector methods. Thus the Wilcox-Lamb equation

$$\dot{P}^W(t) = \left[R + U \frac{1}{B} V\right] P^W(t)$$

$$= R^W P^W(t)$$

has solutions of the form

$$P_n^W(t) = \sum_\mu e^{\mu t} \sum_m (n|\mu)\ (\mu|m)\ P_m(0)$$

where the bras and kets of R^W satisfy respectively the eigenvalue equations

$$(\mu| \left[R + U \frac{1}{\beta} V \right] = \lambda\ (\mu|$$

$$\left[R + U \frac{1}{\beta} V \right] |\mu) = \lambda\ |\mu)$$

When $\lambda = 0$ these equations are identical to the equation satisfied by the exact eigenvectors $< P\lambda_o|$ and $|P\lambda_o >$ of the zero-eigenvalue $\lambda_o = 0$ Bloch equation. Thus the two sets of eigenvectors are equal, apart from a possible normalization constant. But we have already seen that $< Q\lambda_o|$ is the null vector, so that $|\mu_o)$ and $|\lambda_o >$ are actually normalized the same way. We conclude that

$$(n|\mu_o) = < nn|\lambda_o > \quad \text{when} \quad \mu_o = \lambda_o = 0$$

We can readily construct a zero-eigenvalue ket $|\mu_o\}$ after noting that R and U have elements

$$R_{mn} = M_{mn,nn} \qquad U_{m,k\ell} = M_{mn,k\ell}$$

so that, from previously noted summation properties of M we have

$$\sum_m R_{mn} = r_n \qquad \sum_m U_{m,k\ell} = U$$

Thus the ket $(1|$ with unit components

$$(1|m) = 1 \quad \text{for all } m$$

is an eigenket for R and U with zero eigenvalues:

$$(1|R = r \qquad (1|U = C$$

Because the zero eigenvector governs the long-time behavior of $P(t)$ we see that the WL approximation has the correct behavior in the limit of long times:

$$P^W(\infty) = P(\infty)$$

Next consider the first-order WL equation

$$\dot{P}^F(t) = -\left[1 - U\frac{1}{B^2}V\right]^{-1}\left[r + U\frac{1}{B}V\right] P^F(t)$$

$$\equiv \quad R^F P^F(t)$$

We solve this equation, once again, by constructing eigenvectors of the operator R^F. Now note that because R^F has the structure

$$R^F = \left[1 - U\frac{1}{B^2}V\right]^{-1} R^W$$

then any zero-eigenvalue right eigenvector of the Wilcox-Lamb operator R^W is also a zero-eigenvalue eigenvector of R^F:

$$R^F |u_\alpha) = 0 \qquad \text{if} \qquad R^W |u_\alpha) = 0$$

Next observe that, because $(1|U = 0$, the action of $[1 - U\frac{1}{B^2}V]^+$ upon $(1|$ is

$$(1|\left[1 - U\frac{1}{B^2}V\right]^{-1} = (1|$$

Thus we find that $(1|$ is an eigenket of R^F as well as of R^W:

$$(1|R^F = (1|R^W = 0$$

We conclude that R^F and R^W have the same zero-eigenvalue eigenvectors, so that the long-time behavior of both of these master equations is correct:

$$P^F(\infty) = P^W(\infty) = P(\infty).$$