Analytic approach to quantum-mechanical time averages

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We show that the time-averaged density matrix which involves the solution of any Liouville equation with a specified initial condition is also the steady-state solution of an appropriately constructed Bloch equation taken in the weak-damping limit. This leads to new explicit expressions for the time-averaged density matrix which, unlike expressions in general use, give a completely analytic relation between the time average and the initial condition and contain no numerically determined eigenvector components. We apply this approach to driven multilevel systems to find new expressions for the time-averaged level populations in a three-level system. A strong initial-condition dependence is exhibited even for an equally spaced resonantly driven system. Analytic forms specifically showing a Stark-shifted multiphoton resonance and the associated line shape are also derived.

Time-averaged quantum-mechanical density matrices have appeared recently in many diverse applications in the literature including the investigation of driven systems,[1] tracking the flow of probability in intramolecular dynamics,[2] and most recently as a basis-independent measure of chaos.[3] Perhaps of even greater significance is the early work in statistical mechanics which considered time averages as a possible logical precursor for ensemble averages.[4] Despite the growing significance attached to this quantity, it seems not to have been recognized that, for any time-independent Hamiltonian H, the time-averaged density matrix can be written down explicitly in any basis set as a rational analytic function of the Hamiltonian expressed in that basis set.

The time-averaged density matrix $\bar{\rho}$ can be defined by

$$\bar{\rho}=\lim_{T\to\infty}\frac{1}{T}\int_0^T\rho(t)\,dt \ , \tag{1}$$

$$\frac{d\rho}{dt}=\frac{i}{\hbar}[\rho,H]\equiv L\rho \ , \quad \rho(t=0)=\rho^* \ . \tag{2}$$

Evaluating $\bar{\rho}$ presents no problem in the energy basis since the diagonal elements are constant and each off-diagonal element connecting nondegenerate energy states E_q and E_r is a single term oscillating with the energy difference frequency $(E_q-E_r)/\hbar$. With any other set of states, the time dependence of $\rho(t)$ appears expanded out as a sum of both oscillating and constant terms whose coefficients depend on the eigenvector components of H. The usual expressions[1,2] for time-averaged populations result when this expansion for $\rho(t)$ is substituted into Eq. (1), thereby averaging the oscillating terms to zero.

While this approach has been found convenient for many recent applications,[1,2] it has a serious disadvantage from the point of view of analysis. The eigenvector components which occur in it must be determined numerically for most systems of interest. As we will show, such a procedure is unnecessary and possibly undesirable since it could obscure important analytic properties.

To derive expressions for $\bar{\rho}$ which avoid the numerical eigenvalue problem, we begin by pointing out that $\bar{\rho}$ can be expressed in a form that is slightly different from the original definition in Eq. (1),

$$\bar{\rho}=\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\infty e^{-t/\tau}\rho(t)\,dt \ . \tag{3}$$

It is easily verified that applying this new definition to $\rho(t)$ expressed as the usual sum of undamped oscillating terms gives the same result as Eq. (1). What is especially interesting about the new form for $\bar{\rho}$ is that the function of τ, whose limit is taken in Eq. (3), is just $1/\tau$ multiplied by the Laplace transform of ρ ($1/\tau$ being the transform variable). Since H, and therefore L, is independent of time, we can find this transform by applying the Laplace transform operation $\mathfrak{L}$ directly to both sides of Eq. (2). If we let $\rho(\tau)$ be the finite $-\tau$ generalization of $\bar{\rho}$, we find immediately that

$$\left(L-\frac{1}{\tau}\right)\bar{\rho}(\tau)+\frac{1}{\tau}\rho^*=0 \ . \tag{4}$$

The initial condition ρ^* enters the problem in the usual way through the relationship $\mathfrak{L}(d\rho/dt)=(1/\tau)\mathfrak{L}(\rho)-\rho^*$.[5] We can formally solve Eq. (4) for $\bar{\rho}(\tau)$ to obtain

$$\rho(\tau)=(1/\tau)(1/\tau-L)^{-1}\rho^* \ . \tag{5}$$

Defining a time-averaged evolution operator T by

$$\bar{\rho}=T\rho^* \ , \tag{6}$$

we find

$$T=\lim_{\tau\to\infty}(1/\tau)(1/\tau-L)^{-1} \ . \tag{7}$$

This shows right away that the time averages are, as claimed, rational, analytic functions of the Hamiltonian.

The step of taking $\bar{\rho}(\tau)$ for finite τ and then taking the limit $\tau\to\infty$ is essential. If we started out with $1/\tau=0$ in Eq. (4), we would have simply

$$L\bar{\rho}=0 \ , \tag{8}$$

an equation that could have been deduced directly by time averaging both sides of Eq. (2). Clearly, however, L always has more than one eigenvector with eigenvalue zero. Consequently, the solution of Eq. (7) is not unique and only by first finding $\bar{\rho}(\tau)$ and then taking the limit can the proper correspondence between $\bar{\rho}$ and the initial condition ρ^* be established.

The general analytic solution for $\bar{\rho}$ in Eq. (5) is of limited interest from a computational point of view since for an $N\times N$ Hamiltonian it requires inversion of an $N^2\times N^2$ matrix in order to determine $\bar{\rho}$ for arbitrary initial conditions. Even as an analytic tool, Eq. (5) does not automatically lead to explicit expressions whose physical content is obvious. Instead of working with Eq. (5) directly, we can go back a step and take advantage of the analytic possibilities in Eq. (4) in a way that turns out to be simpler. This approach leads us to consider the following Bloch or linear Boltzmann equation

$$\frac{d\rho}{dt}=L\rho+\frac{1}{\tau}(K^*-1)\rho \ , \tag{9}$$

which we have previously used[6–8] to describe the dynamics of a system with Hamiltonian H randomly perturbed by collisions at a frequency $1/\tau$. In this equation, K^* is a collision superoperator[6,7] which we will discuss below. Now comparing Eq. (9) with Eq. (4), we see that if we substitute ρ^* for $K^*\rho$ in Eq. (9), Eq. (4) is just the steady-state equation for Eq. (9). Thus the steady state of this Bloch equation is the $\bar{\rho}(\tau)$ needed to solve Eq. (4) and we can take its $\tau\to\infty$ limit to find the infinite time average. Using ρ_{ss} to denote the steady-state solution of Eq. (9), we can summarize the foregoing discussion in the following equation:

$$\lim_{\tau\to\infty}\rho_{ss}=T\rho^*\equiv\bar{\rho} \ . \tag{10}$$

We note that since the collision operator K^* makes the state after a collision (i.e., $K^*\rho=\rho^*$) independent of the state ρ before the collision, it may be thought of as a generalization of previously discussed "strong collision"[9] operators.

The reason that identifying the time-averaged quantity $\bar{\rho}$ with the low-pressure $(1/\tau\to 0)$ limit of ρ_{ss} [Eq. (10)] leads to a useful reformulation of the time-averaging problem is that the Bloch equation can often be reduced to a much simpler set of equations.[7,10] To bring the present strong collision result into the same physical language as the earlier work,[6,7] we note that a strong collision operator K^*, where the associated postcollision density matrix ρ^* is diagonal, is formally equivalent to the following definition of K as a superoperator[6,7] on ρ,

$$K_{ij,kl}=P_{j\leftarrow l}\delta_{ij}\delta_{kl} \ , \tag{11}$$

provided we choose $P_{j\leftarrow l}$, the probability that a system in state l before a collision will be in state j after the collision, so that $P_{j\leftarrow l}=\rho^*_{jj}$ independent of the initial state l. Previous work has shown that for arbitrary time-independent Hamiltonians[10] and arbitrary collision operators[7] the solutions of the Bloch equation [Eq. (9)] can be found by first eliminating the off-diagonal density-matrix elements to obtain a generalized master equation (GME)[7]

$$\frac{d\rho_{jj}}{dt}=\sum_{k\neq j}\left[W_{jk}(\lambda)+\frac{P_{j\leftarrow k}}{\tau}\right]\rho_{kk}-\left[W_{kj}(\lambda)+\frac{P_{k\leftarrow j}}{\tau}\right]\rho_{jj} \ . \tag{12}$$

The parameter λ (corresponding to a Bloch equation eigenvalue) is either set to zero, and the steady-state solution found by solving Eq. (12) for its steady state, or determined self-consistently to find solutions proportional to $\exp(\lambda t)$ for $\lambda\neq 0$. The $N\times N$ problem involved in solving the GME for its single steady-state eigenvector represents a substantial advantage over the direct inversion of $(1/\tau-L)$ in Eq. (5) or the matrix diagonalization in the usual approach, provided the transition coefficients $W_{ij}(\lambda)$ can be found without too much work. When H is tridiagonal, we have found both algebraic[7] and diagramatic[8] techniques that permit a systematic determination of W with a minimum amount of work. Since the coupling in systems of physical interest is often restricted in some way (for example, exchange of quanta may be restricted in intramolecular vibrational coupling[11,12]), useful generalizations of these techniques may well be possible.

While Eq. (10) involving the strong collision model is sufficient for calculating time averages, it is interesting to note that there is a connection between the time-averaged evolution operator T and the Bloch equation steady state for other collision models. If K is any collision operator defined by Eq. (11), then a more general kind of argument can be made[13] reexpressing Eq. (9) as an integral equation to show that

$$\rho_{ss}(\tau\to\infty)=TK\rho_{ss}(\tau\to\infty) \ . \tag{13}$$

Equation (10) is obviously a special case of this relationship, where $K\rho_{ss}=\rho^*$.

Now we consider a specific problem for which our approach leads to new analytic expressions. We take a three-level atom with driving terms proportional to a field $A\sin\chi t$. Making the rotating wave approximation leads to a time-independent effective Hamiltonian[14] with terms proportional to $\alpha_{01}A/2\hbar$ and $\alpha_{12}A/2\hbar$ coupling adjacent pairs of atomic energy levels. The quantities of physical interest are the time-averaged populations of these energy levels even though, because of the coupling terms, these are not energy eigenstates of the effective Hamiltonian. Now, applying the GME, we obtain with very little effort,[7] the following expressions for the radiative-induced transition coefficients $W_{ij}(\lambda=0)$ in Eq. (12):

$$W_{01}=W_{10}=\frac{2\beta_1^2}{D\tau}\left[\left(\frac{1}{\tau^2}+\Delta_{12}^2\right)\left(\frac{1}{\tau^2}+\Delta_{02}^2\right)+\beta_1^4-\beta_2^4+2\beta_1^2\left(\frac{1}{\tau^2}-\Delta_{12}\Delta_{02}\right)+\beta_2^2(\Delta_{12}^2+\Delta_{01}\Delta_{12}+\Delta_{01}\Delta_{02}+\Delta_{12}\Delta_{02})\right] ,$$

$$W_{12}=W_{21}=\frac{2\beta_2^2}{D\tau}\left[\left(\frac{1}{\tau^2}+\Delta_{01}^2\right)\left(\frac{1}{\tau^2}+\Delta_{02}^2\right)+\beta_2^4-\beta_1^4+2\beta_2^2\left(\frac{1}{\tau^2}-\Delta_{01}\Delta_{02}\right)+\beta_1^2(\Delta_{01}^2+\Delta_{01}\Delta_{12}+\Delta_{01}\Delta_{02}+\Delta_{12}\Delta_{02})\right] ,$$

$$W_{02}=W_{20}=\frac{2\beta_1^2\beta_2^2}{D\tau}\left(\frac{1}{\tau^2}-\Delta_{01}\Delta_{12}-\Delta_{01}\Delta_{02}-\Delta_{12}\Delta_{02}+\beta_1^2+\beta_2^2\right) , \tag{14}$$

where

$$D=\left(\frac{1}{\tau^2}+\Delta_{01}^2\right)\left(\frac{1}{\tau^2}+\Delta_{12}^2\right)\left(\frac{1}{\tau^2}+\Delta_{02}^2\right)+2\beta_1^2\left(\frac{1}{\tau^2}+\Delta_{01}\right)\left(\frac{1}{\tau^2}-\Delta_{12}\Delta_{02}\right)+2\beta_2^2\left(\frac{1}{\tau^2}+\Delta_{12}^2\right)\left(\frac{1}{\tau^2}-\Delta_{01}\Delta_{02}\right)$$
$$+\beta_1^4\left(\frac{1}{\tau^2}+\Delta_{01}^2\right)+\beta_2^4\left(\frac{1}{\tau^2}+\Delta_{12}^2\right)+2\beta_1^2\beta_2^2\left(\frac{1}{\tau^2}+\Delta_{01}\Delta_{12}\right) , \quad \beta_i=\alpha_{i-1,i}A/2\hbar .$$

The Δ's are detunings from resonance given in terms of the atomic energies E_i by

$$\Delta_{jk}=(k-j)\chi-(E_k-E_j)/\hbar .$$

Since the development leading to Eq. (12) has reduced the problem of finding $\bar{\rho}$ for arbitrary initial conditions to finding the steady-state solution of Eq. (12) with $P_{i\leftarrow j}$'s chosen to be a strong collision model, the expressions in Eq. (14) provide all that is needed to determine $\bar{\rho}$ for any initial conditions and for any choice of the coupling or detuning parameters. If we have equally spaced energy levels driven on resonance (all Δ's $=0$), finding the appropriate ρ_{ss}'s for Eq. (12) and taking the limit $\tau\rightarrow\infty$ leads to the following remarkably simple results:

$$T_{00,11}=T_{11,00}=\tfrac{1}{2}\beta_1^2/(\beta_1^2+\beta_2^2) ,$$
$$T_{11,22}=T_{22,11}=\tfrac{1}{2}\beta_2^2/(\beta_1^2+\beta_1^2) , \tag{15}$$
$$T_{00,22}=T_{22,00}=\tfrac{3}{2}\beta_1^2\beta_2^2/(\beta_1^2+\beta_2^2)^2 .$$

These expressions show that the averaged populations in different levels are unequal and generally strongly dependent on initial conditions. This dependence is of fundamental interest in connection with time averages in general because of their connection with the equilibrium problem[4] in statistical mechanics. The time-averaged solutions in driven systems have generally been considered in the context of single and multiphoton resonances.[1] For the case of a multiphoton resonance ($\Delta_{01}\approx-\Delta_{12}$, $|\Delta_{01}|\gg\beta_1,\beta_2$), our expression for the critical $0\rightarrow2$ population transfer reduces to

$$T_{22,00}\cong\frac{2\beta_1^2\beta_2^2/\Delta_{01}^2}{4\beta_1^2\beta_2^2/\Delta_{01}^2+[\Delta_{02}-(\beta_1^2-\beta_2^2)/\Delta_{01}]^2} ,$$

with $T_{00,00}\approx1-T_{22,00}$. The condition for optimum transfer of population ($T_{22,00}=\frac{1}{2}$) occurs, as should be expected, at the Stark-shifted frequency $(\beta_1^2-\beta_2^2)/\Delta_{01}$ and has a "power-broadening" width proportional to the effective two-level Rabi frequency $\beta_1\beta_2/\Delta_{01}$.[15]

Our approach to time averages has permitted us to write out analytic forms for time-averaged level populations without ever having to consider the eigenvalues or eigenvectors of the Hamiltonian. A systematic investigation of time averages may even shed new light on the logical foundations of statistical mechanics and it is hoped that the approach outlined will be useful for this purpose.

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[1]H. W. Galbraith and J. R. Ackerhalt, Opt. Lett. 3, 152 (1978); C. D. Cantrell and H. W. Galbraith, Opt. Commun. 21, 374 (1977).
[2]K. S. J. Nordholm and S. A. Rice, J. Chem. Phys. 61, 203 (1974); K. G. Kay, *ibid.* 72, 5955 (1980); E. J. Heller and M. J. Davis (unpublished).
[3]E. Thiele (unpublished).
[4]J. von Neumann, Z. Phys. 57, 30 (1929); N. G. van Kampen, Physica (Utrecht) 20, 603 (1954); I. E. Farquhar, *Ergodic Theory in Statistical Mechanics* (Interscience, London, 1964).
[5]J. Mathews and R. L. Walker, *Mathematical Methods of Physics* (Benjamin, New York, 1970), p. 110.
[6]M. F. Goodman and E. Thiele, Phys. Rev. A 5, 1355 (1972).
[7]J. Stone, E. Thiele, and M. F. Goodman, J. Chem. Phys. 59, 2909 (1973).
[8]J. Stone and M. F. Goodman, Phys. Rev. A 18, 2618 (1978).
[9]R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).
[10]L. R. Wilcox and W. E. Lamb, Jr., Phys. Rev. 119, 1915 (1960).
[11]J. Stone, E. Thiele, and M. F. Goodman, J. Chem. Phys. 75, 1712 (1981).
[12]H. W. Galbraith and J. R. Ackerhalt, Chem. Phys. Lett. 84, 458 (1981).
[13]J. Stone, M. F. Goodman, and E. Thiele (unpublished).
[14]S. Mukamel and J. Jortner, Chem. Phys. Lett. 40, 150 (1976).
[15]J. C. Diels, J. Stone, S. Besnainou, M. F. Goodman, and E. Thiele, Opt. Commun. 37, 11 (1981); D. M. Larsen and N. Bloembergen, *ibid.* 17, 254 (1976).