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Evolution operator for a multilevel system in a continuous-wave laser field

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The assumed existence of a time-independent Kubo-type operator renders possible an analytic expression for the evolution operator of a quantized system. For a multilevel system dipole interacting with a continuous-wave laser, the realization of a suitable Kubo-type transformation through an algebraic algorithm may require that the Hamiltonian operator of the system be simplified through, say, the imposition of the rotating-wave approximation and/or the appeal to transition dipole selection rules that validate the neglect of unimportant couplings. The resultant sparse Hamiltonian operator is arbitrarily constructed on the basis of the near-resonant laser coupling of the ground state to the excited states, but without direct appeal to the magnitude of the dipole coupling strength parameters. The implementation and associated computational aspects of a resolvent method for evaluating the evolution operator is discussed and illustrated through the calculation of the transition probabilities for the excitation of an anharmonic oscillator model of the CH stretch in CD_3H.

I. INTRODUCTION

In this paper we are concerned with the laser-induced multiphoton excitation of an isolated molecule under collision-free conditions. Technological interest in the development of isotope separation processes creates the engineering design requirement for realistic simulations of the underlying photoexcitation and photodissociation dynamics of polyatomic molecules in coherent infrared laser fields whose intensities range up to about 100 $\mathrm{GW\,cm^{-2}}$. The dynamical equation of motion is the Schrödinger equation for the amplitudes of the various states of the molecular system in a suitable basis, usually the spectroscopic eigenenergy basis. With the field treated classically, the Hamiltonian operator of the system is time dependent. There is no analytic solution available for the state amplitude equation of motion of a polyatomic molecule in an intense coherent laser field, and one must resort to the use of efficient computational schemes in simulating the multiphoton dynamical processes. Present day[1] understanding of multiphoton processes in polyatomic molecules distinguishes between laser intensity-dependent coherent nonresonant excitation in the low-energy discrete states and laser fluence-dependent incoherent resonant excitation in the higher-energy quasicontinuum of rovibrational states; eventually the molecule may acquire sufficient energy to undergo unimolecular decomposition through various dissociative channels. Isotopic selectivity is attained by way of the laser power-dependent excitation of a vibrational mode through several near-harmonic molecular energy levels and results in the appearance of multiphoton resonances and saturation behavior in strict adherence to the prevailing selection rules; appeal is made to such mechanisms as power broadening, rotational band structure, and anharmonic splitting of vibrational levels in order to compensate for the increasing detuning between the molecule and the field until mechanical anharmonicity gives rise to a quasicontinuum of rovibrational states which have no significant isotopic dependencies. Due to the low efficiencies of laser sources and the possible need for large throughput, photon economics during the initial stages of multiphoton excitation is important for achieving high isotope separation factors, irrespective of whether or not dissociation through desirable channels is ultimately attained. Here we discuss the application of a resolvent method for calculating the multiphoton excitation transition probabilities of the low-energy structured spectrum of a vibrational mode up to the onset of the quasicontinuum.

Dyson's formula for the evolution operator[2,3] $U(t)$ which formally expresses the time development of a quantized system from its initial $|\Psi(0)\rangle$ to its final state $|\Psi(t)\rangle = U(t)|\Psi(0)\rangle$ within the interaction picture and in accordance with the Schrödinger equation

$$\frac{\partial}{\partial t}|\Psi(t)\rangle = -iH(t)|\Psi(t)\rangle \,, \tag{1a}$$

where $H(t)$ is the time-dependent Hamiltonian operator, does not represent a practical prescription for the construction of $U(t)$ for arbitrary times. Of course if $[H(t'),H(t'')]=0$ then $U(t)=\exp[-i\int_0^t ds\,H(s)]$. One can capitalize on this fact if somehow the time dependence of $H(t)$ could be eliminated. This was done by Einwohner, Wong, and Garrison[4] in their consideration of the dipole interaction of a many-level system with multiple lasers; after first invoking the resonance-constrained global rotating-wave approximation[5] (RWA), they employed a unitary transformation to eliminate all remaining time dependence in the modified Hamiltonian operator, the form of the transformation being justified on the basis of a graph-theoretic argument. Whaley and Light[5] introduced a unitary rotating-frame transformation (RFT) which defines a representation wherein H is time independent if one applies the global RWA (Ref. 5) and neglects the residual time-dependent couplings. It has recently been pointed[6(a)] out that the RFT is equivalent to the quasiresonant approximation (QRA) introduced by Quack.[6(b)] In an earlier paper,[7] Freed also recognized the need for a transformation to an interaction picture which results in a time-invariant dynamical equation of motion that can be easily integrated. This was done in specific applications to three-level double-resonance and eight-level triple-resonance systems by appropriate choice of a phase-factoring transformation (PFT).

This paper has a twofold purpose. First, to show how a Kubo-type transformation can be determined through an algebraic algorithm, thereby allowing one to define a reference frame in which the Hamiltonian operator of a multilevel system dipole interacting with an oscillating field is time independent. This approach unifies the three ostensibly different PFT, QRA, and RFT procedures. If the approach presented were merely to reformulate known—albeit equivalent—procedures then not much would be gained. However, the unifying approach, through its algebraic algorithm, reveals a common basic weakness in these procedures through their sole reliance on resonance detunings in the selection of the most probable path for multiphoton excitation. A secondary intent is to promote the usage of a resolvent method for evaluating the evolution operator in the Kubo picture.

The paper is organized as follows: In Sec. II A we show how the assumed existence of a time-independent Kubo-type operator governing the time development of the Hamiltonian operator of an arbitrary quantized system allows one to express the evolution operator as the product of a pair of matrix exponentials. The uniqueness of the Kubo-type operator is also discussed. A resolvent method suitable for the evaluation of these matrix exponentials, and hence the transition probability amplitudes, is described in Sec. II B and its implementation and associated computational aspects are discussed in Sec. II C. In the context of a multilevel system dipole interacting with a continuous-wave (cw) laser, we show in Sec. III A how to determine a suitable Kubo-type operator through an algebraic algorithm, subject to the imposition of the RWA and/or the appeal to transition dipole selection rules that validate the neglect of unimportant couplings. As an illustrative application of both the algebraic algorithm for the determination of the Kubo-type transformation and the resolvent scheme for computing the evolution operator, we calculate in Sec. III B the transition probabilities for the excitation of an anharmonic oscillator model of the CH stretch in CD_3H. There is a brief concluding summary in Sec. IV. Atomic units are used throughout the paper unless otherwise indicated.

II. FORMAL ANALYSIS

A. State amplitude equation of motion

The evolution of the state amplitude matrix $\mathbf{c}(t)$ of a multilevel (N, say) system is governed by the Schrödinger equation

$$\dot{\mathbf{c}}(t)=\mathbf{C}(t)\mathbf{c}(t) \ . \tag{1b}$$

Here $\mathbf{c}(t)$ is an N-vector whose components $c_k(t)=\langle k \mid \Psi(t)\rangle$ are the probability amplitudes for the stationary eigenstates $\mid k\rangle$, $k=1,2,\ldots,N$ of the isolated system and $\mathbf{C}(t)=-i\mathbf{H}(t)$, where $\mathbf{H}(t)$ is an $N\times N$ matrix representation of the system's Hamiltonian operator.

The Kubo-type operator $\mathbf{A}^x$ is formally defined[8] as $\mathbf{A}^x\equiv[\mathbf{A},\ ]$ and has the properties

$$\mathbf{A}^x\mathbf{B}=[\mathbf{A},\mathbf{B}] \tag{2a}$$

and

$$\exp(\mathbf{A}^x\alpha)\mathbf{B}=\exp(\mathbf{A}\alpha)\mathbf{B}\exp(-\mathbf{A}\alpha) \ , \tag{2b}$$

where $\mathbf{B}$ is an arbitrary operator and α is an arbitrary scalar.

Suppose there exists an operator $\mathbf{A}^x$ such that

$$\dot{\mathbf{C}}(t)=\mathbf{A}^x\mathbf{C}(t) \ , \tag{3}$$

where $\mathbf{A}^x$ is independent of time. Thus, $\mathbf{C}(t)=\exp(\mathbf{A}^x t)\mathbf{C}(0)$ which with Eq. (2b) allows one to rewrite Eq. (1b) as

$$\dot{\mathbf{c}}(t)=\exp(\mathbf{A}t)\mathbf{C}(0)\exp(-\mathbf{A}t)\mathbf{c}(t) \ . \tag{4}$$

Under the transformation $\tilde{\mathbf{c}}(t)=\exp(-\mathbf{A}t)\mathbf{c}(t)$, Eq. (4) becomes

$$\dot{\tilde{\mathbf{c}}}(t)=[\mathbf{C}(0)-\mathbf{A}]\tilde{\mathbf{c}}(t) \ , \tag{5}$$

from which it follows that $\tilde{\mathbf{c}}(t)=\exp\{[\mathbf{C}(0)-\mathbf{A}]t\}\tilde{\mathbf{c}}(0)$. Hence

$$\mathbf{c}(t)=\mathbf{U}(t)\mathbf{c}(0) \ , \tag{6}$$

where the evolution operator $\mathbf{U}(t)$ is given in terms of $\mathbf{A}$ as

$$\mathbf{U}(t)=\exp(\mathbf{A}t)\exp\{[\mathbf{C}(0)-\mathbf{A}]t\} \ . \tag{7}$$

Thus, for the initial conditions $\mathbf{c}(0)$, the evolution operator $\mathbf{U}(t)$ for the first-order system in Eq. (1b) is given by Eq. (7) provided the time-independent Kubo-type operator $\mathbf{A}^x$ exists and $\exp(\mathbf{A}^x t)$ is itself the evolution operator of $\mathbf{C}(t)=-i\mathbf{H}(t)$ for the initial conditions $\mathbf{C}(0)$ in accordance with Eq. (3). When $\mathbf{H}(t)$ is Hermitian, $\mathbf{C}^{\dagger}(t)=-\mathbf{C}(t)$ and it is easy to show that if $\mathbf{A}$ is also anti-Hermitian then $\mathbf{U}(t)$ as given in Eq. (7) is unitary for all t. The existence of $\mathbf{A}$ permits one to factor $\mathbf{U}(t)$ into the product of exponentials of *time-independent* operators.

Using Eqs. (2a) and (3) as necessary, the exponentials in Eq. (7) can be united by the Baker-Campbell-Hausdorff formula[9] to give

$$\mathbf{U}(t)=\exp\{\mathbf{C}(0)t+\tfrac{1}{2}\dot{\mathbf{C}}(0)t^2+\tfrac{1}{12}\ddot{\mathbf{C}}(0)t^3 + \tfrac{1}{24}[\dot{\mathbf{C}}(0),\mathbf{C}(0)]t^3+\cdots\} \ . \tag{8}$$

The higher-order terms are available,[10] but the expansion is not unique due to the existence of various relationships between nested commutators of operators.

For completeness we mention that the foregoing is equally applicable to the Liouville equation[8(a)] describing the time development of an ensemble of N-level systems, namely,

$$\dot{\rho}(t)=-i[\mathbf{L}(t)+i\mathbf{R}]\rho(t) \ , \tag{9}$$

where $\rho(t)$, $\mathbf{L}(t)=\mathbf{H}^x(t)$, and $\mathbf{R}$ are the $N\times N$ matrix representations of the density, Liouville, and relaxation operators, respectively, in the eigenenergy basis; the

Kubo-type operator $\mathbf{A}^x$ governs the evolution of $\mathbf{L}(t)+i\mathbf{R}$ from its initial free-streaming value $\mathbf{L}(0)+i\mathbf{R}$.

One of the difficulties in the application of Eq. (7) is the assumed existence of $\mathbf{A}$. We offer no existence criteria for $\mathbf{A}$, anymore than quantum theory supplies Hamiltonian operators. It may be that a Kubo-type operator $\mathbf{A}^x$ governing the evolution of the Hamiltonian operator of a quantized system in accordance with

$$\dot{\mathbf{H}}(t)=\mathbf{A}^x\mathbf{H}(t) , \tag{10}$$

cannot be found unless $\mathbf{H}(t)$ is simplified in some physically justified way. Equation (10) is valid if and only if $\mathbf{H}(t)$ converges to its Maclaurin expansion for all t; this will clearly not be so in the general case. In the context of a multilevel system dipole interacting with a near-resonant laser, we will discuss in Sec. III A how retaining just the proresonant part of $\mathbf{H}(t)$ allows one to determine a suitable Kubo-type transformation matrix. However, we first give in the following the details of a resolvent method which is well suited for evaluating the exponential matrices appearing in Eq. (7).

B. Leverrier-Bateman resolvent method

Herein reference to argument free $\mathbf{C}$ will signify $\mathbf{A}$ or $\mathbf{C}(0)-\mathbf{A}$, as necessary. If the coefficient matrix $\mathbf{C}$ in Eq. (1b) were time independent then the solution for initial conditions $\mathbf{c}(0)$ is simply

$$\mathbf{c}(t)=\exp(\mathbf{C}t)\mathbf{c}(0) , \tag{11}$$

as follows by direct integration. Alternatively, one can Laplace transform Eq. (1b) to s space to obtain

$$\mathbf{c}(s)=(s\mathbf{I}-\mathbf{C})^{-1}\mathbf{c}(0) . \tag{12}$$

Formally inverting Eq. (12) gives

$$\mathbf{c}(t)=\frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} ds\, \exp(st)(s\mathbf{I}-\mathbf{C})^{-1}\mathbf{c}(0) , \tag{13}$$

where α is an arbitrary real number to be chosen so that all singularities of the integrand lie to the left of $s=\alpha$ and the integration is to be performed along the straight line $\mathrm{Re}(s)=\alpha$ parallel to the imaginary axis. From Eqs. (12) and (13) one has the standard expression[11] for $\exp(\mathbf{C}t)$ as the inverse Laplace transform of the resolvent $(s\mathbf{I}-\mathbf{C})^{-1}$, namely,

$$\exp(\mathbf{C}t)=\frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} ds\, \exp(st)(s\mathbf{I}-\mathbf{C})^{-1} . \tag{14}$$

To evaluate the integral in Eq. (14) we make use of Leverrier's expression[12] for $(s\mathbf{I}-\mathbf{C})^{-1}$ as given by

$$(s\mathbf{I}-\mathbf{C})^{-1}=\sum_{l=1}^{N} s^{N-l}\mathbf{Z}_l/\det(s\mathbf{I}-\mathbf{C}) , \tag{15}$$

where the $\mathbf{Z}_l$'s are $N\times N$ matrices that are independent of s and will be discussed further in what follows, and the partial fraction expansion of $s^{N-l}/\det(s\mathbf{I}-\mathbf{C})$ as given by

$$s^{N-l}/\det(s\mathbf{I}-\mathbf{C})=\sum_{i=1}^{r}\sum_{k=1}^{n_i}\frac{d^{n_i-k}}{ds^{n_i-k}}\left[\frac{s^{N-l}}{\prod\limits_{m\neq i}^{r}(s-\lambda_m)^{n_m}}\right]_{s=\lambda_i}\Bigg/(s-\lambda_i)^k(n_i-k)! , \tag{16}$$

where λ_i, $i=1,\ldots,r$ are the distinct eigenvalues of $\mathbf{C}$ with corresponding multiplicities n_i so that $\sum_{i=1}^{r}n_i=N$. Substituting Eqs. (15) and (16) into Eq. (14) and evaluating the integral through use of the residue theorem gives

$$\exp(\mathbf{C}t)=\sum_{l=1}^{N}\sum_{i=1}^{r}\sum_{k=1}^{n_i} t^{k-1}\exp(\lambda_i t)a_{ikl}(\lambda_i)\mathbf{Z}_l , \tag{17}$$

where

$$a_{ikl}(\lambda_i)=\frac{d^{n_i-k}}{ds^{n_i-k}}\times\left[\frac{s^{N-l}}{\prod\limits_{m\neq i}^{r}(s-\lambda_m)^{n_m}}\right]_{s=\lambda_i}\Bigg/(k-1)!(n_i-k)! . \tag{18}$$

If $r=N$ then $n_i=1$ for all $i=1,\ldots,N$, and Eq. (17) reduces to

$$\exp(\mathbf{C}t)=\sum_{l=1}^{N}\exp(\lambda_l t)\mathbf{N}_l , \tag{19}$$

where the $\mathbf{N}_l$'s are $N\times N$ Bateman coefficient matrices[13] given by

$$\mathbf{N}_l=\sum_{i=1}^{N}\lambda_l^{N-i}\mathbf{Z}_i\Bigg/\prod_{i\neq l}(\lambda_l-\lambda_i) . \tag{20a}$$

The $\mathbf{Z}_i$'s are generated through Faddeev's and Sominskii's modification[12(b)] of Leverrier's algorithm[12(a)] and are given recursively for $i=2,\ldots,N$ as

$$\mathbf{Z}_i=\mathbf{C}\mathbf{Z}_{i-1}+\theta_{i-1}\mathbf{I} , \tag{20b}$$

with $\mathbf{Z}_1=\mathbf{I}$, and the scalar θ_i's are given for $i=1,\ldots,N$ as

$$i\theta_i=-\mathrm{Tr}(\mathbf{C}\mathbf{Z}_i) . \tag{20c}$$

Assuming that the time-independent matrices $\mathbf{A}$ and $\mathbf{C}(0)-\mathbf{A}$ have distinct eigenvalues, one can substitute the form of Eq. (19) into (7), and for the initial conditions $\mathbf{c}(0)$, one obtains

$$P_{kk}(t)=\sum_{\substack{l,m,r,s,\\ l',m',r',s'=1}}^{N} \exp[(\lambda_l+\widetilde{\lambda}_m+\lambda_{l'}^{*}+\widetilde{\lambda}\,_{m'}^{*})t]N_{kr,l}N_{kr',l'}^{*}\widetilde{N}_{rs,m}\widetilde{N}\,_{r's',m'}^{*}c_s(0)c_{s'}^{*}(0) \tag{21a}$$

as the transition probability $|\,c_k(t)\,|^2$ for excitation to state $|\,k\,\rangle$. If the system is characterized by a uniform relaxation time τ then the Laplace time-averaged transition probability

$$P_{kk}^{\tau}=\tau^{-1}\int_0^{\infty} dt\,\exp(-t/\tau)P_{kk}(t)\ ,$$

where $P_{kk}^{\tau}\rightarrow P_{kk}(0)$ as $\tau\rightarrow 0^{+}$ and $P_{kk}^{\tau}\rightarrow P_{kk}(\infty)$ as $\tau\rightarrow\infty$, is given by

$$P_{kk}^{\tau}=\sum_{\substack{l,m,r,s,\\ l',m',r',s'=1}} N_{kr,l}N_{kr',l'}^{*}\widetilde{N}_{rs,m}\widetilde{N}\,_{r's',m'}^{*}c_s(0)c_{s'}^{*}(0)/[1-\tau(\lambda_l+\widetilde{\lambda}_m+\lambda_{l'}^{*}+\widetilde{\lambda}\,_{m'}^{*})]\ . \tag{21b}$$

In Eq. (21) the quantities (eigenvalues and matrix elements of Bateman matrices) without tildes pertain to **A** while those with tildes pertain to **C**(0) − **A**. Similarly, using the form of Eq. (17) in (7) one can generate the unwieldy generalizations of $P_{kk}(t)$ and P_{kk}^{τ} which allow for the confluence of eigenvalues of **A** and/or **C**(0) − **A**. There follows a discussion of the numerical aspects of the Leverrier-Bateman algorithm and its implementation.

C. Computational aspects

Implementation of the Leverrier-Bateman resolvent scheme on either a mainframe machine or a personal microcomputer is easily accomplished; indeed the FORTRAN code used to perform the numerical applications discussed in Sec. III contains less than 300 executable statements. It is straightforward to generate the eigenvalues of **A** and **C**(0) − **A** using the efficient routines available in the IMSL (International Mathematical and Statistical Library) package[14(a)] for both mainframe and microcomputer implementations, or the equivalent routines in the EISPACK library[14(b)] for mainframe machines. The precision with which these eigenvalues are computed imposes a limitation on the extent of the time scale over which the time-resolved transition probability $P_{kk}(t)$ can be accurately evaluated. As given in Eq. (21a), $P_{kk}(t)$ is a superposition of N terms oscillating at incommensurate frequencies; provided the Hamiltonian operator of the system is self-adjoint and periodic in time, $P_{kk}(t)$ is almost periodic[15(a)] and returns[15(b)] arbitrarily close to its initial value infinitely often. The phenomenological relaxation time τ is generally sufficiently short to mitigate the requirement for $P_{kk}(t)$ at long times where inaccuracies in the computed eigenvalues begin to be manifested; the time-averaged transition probability P_{kk}^{τ} is more amenable to measurement and its evaluation through Eq. (21b) is insensitive to the precision of the computed eigenvalues.

The primary difficulty with the resolvent scheme lies with the evaluation of the expansion coefficients $a_{ikl}(\lambda_i)$ given in Eq. (18), in the event that the confluence of eigenvalues is an underlying structural feature of **A** and/or **C**(0) − **A**. To appreciate this we may rewrite Eq. (18) as

$$a_{ikl}(\lambda_i)=\frac{1}{(k-1)!}\sum_{m\neq i}^{r}\prod_{k'\neq m}^{r}(\lambda_m-\lambda_{k'})\prod_{l'=0}^{n_i-k}\frac{1}{l'!(n_i-k-l')}\frac{d^{l'}}{ds^{l'}}(s^{N-l})_{s=\lambda_i}\frac{d^{n_i-k-l'}}{ds^{n_i-k-l'}}[(s-\lambda_m)^{-n_m}]_{s=\lambda_i}\ , \tag{22}$$

a form which highlights the numerical instability in $a_{ikl}(\lambda_i)$, particularly if N is large and r is small. Thus, for close or widely varying eigenvalues the product of differences in eigenvalues in Eq. (22) will be subject to large round-off error. Also, even after differentiation, both s^{N-l} and $(s-\lambda_m)^{-n_m}$ are potentially problematic if N and n_m are large; thus, if $\lambda_i \ll 1$ then the former factor is very small while if λ_i is close to λ_m then the latter factor is very large. However, from Eq. (17) one can easily derive the sum rule

$$\mathbf{C}^m=\sum_{i=1}^{r}[\mathbf{N}_i^{(m)}(0)+\lambda_i^m\mathbf{N}_i(0)] \tag{23a}$$

for $m=0,1,\ldots$, where the $\mathbf{N}_i(t)$'s are time-dependent generalizations of the Bateman matrices given by

$$\mathbf{N}_i(t)=\sum_{k=1}^{n_i}t^{k-1}\sum_{l=1}^{N}a_{ikl}(\lambda_i)\mathbf{Z}_l\ , \tag{23b}$$

and $\mathbf{N}_i^{(m)}(t)$ is the mth derivative of $\mathbf{N}_i(t)$ with respect to time. For m not too large so that $\mathbf{C}^m$ can be reliably evaluated through matrix multiplication, Eq. (23a) serves as a check on the accuracy of computed $\mathbf{N}_i(t)$'s. The $\mathbf{Z}_l$'s in Eq. (23b) can be calculated through use of Leverrier's algorithm given in Eqs. (20b) and (20c).

In the absence of degeneracy among the eigenvalues of **A** and/or **C**(0) − **A**, the $\mathbf{N}_i$'s given in Eq. (23b) become time independent, reducing to the Bateman matrices given in Eq. (20a), and are readily evaluated through use of Leverrier's algorithm for the $\mathbf{Z}_l$'s as given in Eqs. (20b) and (20c). Furthermore, the sum rule in Eq. (23a) reduces to

$$\mathbf{C}^m=\sum_{l=1}^{N}\lambda_l^m\mathbf{N}_l \tag{24a}$$

for $m=0,1,\ldots$. As an additional check on the accuracy of computed $\mathbf{N}_l$'s one can test the extent to which their projection and idempotent properties[11(a)] are fulfilled, viz.,

$$\mathbf{N}_k\mathbf{N}_l=0 \quad \text{if } k\neq l \ , \tag{24b}$$

and

$$\mathbf{N}_k^m=\mathbf{N}_k \quad \text{for } m \text{ any positive integer} \ , \tag{24c}$$

respectively.

The Leverrier scheme is used to evaluate the **Z**'s required in Eq. (20a), defining the Bateman matrices in the absence of confluent eigenvalues, or in Eq. (23b), defining the time-dependent generalizations of the Bateman matrices for the situation in which **A** and/or $\mathbf{C}(0)-\mathbf{A}$ have degenerate eigenvalues. Besides the implicit checks on the computed **Z**'s provided through Eq. (23a) or (24), the condition[11(a)]

$$\mathbf{C}\mathbf{Z}_N+\theta_N\mathbf{I}=0 \tag{25}$$

affords a further and more explicit check on the performance of the algorithm. Degeneracy among the eigenvalues of **C** is not a direct consequence of degeneracy among the stationary eigenstates $|\,k\,\rangle$, $k=1,2,\ldots,N$.

In Sec. III we will apply the Leverrier-Bateman resolvent method in evaluating the transition probabilities for the excitation of a vibrational mode of a polyatomic molecule, but before doing so we will discuss how one obtains a suitable Kubo-type transformation for a multilevel system dipole interacting with a cw laser.

III. DISCUSSION

A. Determination of the Kubo-type transformation

Formally[8(b)] the time-independent Kubo-type operator $\mathbf{A}^x$ is the infinitesimal generator of a one parameter (t) group of strongly continuous operators $\exp(\mathbf{A}^x t)$ associated with the evolution Eq. (3) for $\mathbf{C}(t)=-i\mathbf{H}(t)$. For an arbitrary N-level system $\mathbf{A}^x$, through Eq. (3), *defines* a reference frame in which the effective Hamiltonian operator of the system is $-i[\mathbf{C}(0)-\mathbf{A}]$. In the original representation, the evolution operator $\mathbf{U}(t)$ is given in Eq. (7) as the product of exponentials of time-independent operators involving **A** and $\mathbf{C}(0)$. No appeal was made to the form of $\mathbf{H}(t)$ except for noting that if it is self-adjoint then an anti-Hermitian matrix **A** guarantees the unitarity of the evolution operator. In view of Eq. (8), the evolution operator, and hence the density matrix, are formally independent of the explicit nature of **A**. Whereas Eq. (3) formally defines **A**, it also constitutes an algorithm for the determination of **A**; the N^2 unknown matrix elements of **A** are given unambiguously as the solution to the system of N^2 inhomogeneous linear algebraic equations

$$\dot{\mathbf{C}}(0)=[\mathbf{A},\mathbf{C}(0)] \ . \tag{26}$$

Consequently, Eq. (3) both defines a reference frame where the Hamiltonian operator is rendered constant, and supplies an algorithmic scheme for the determination of the transformation matrix to that frame.

In order to illustrate the foregoing analysis we consider the dipole interaction of an N-level system with a classical electric field $E(t)=E^0\cos(\omega t)$, of constant field strength E^0, frequency ω, and arbitrarily polarized in the z direction. Within the global RWA (Ref. 5) the interaction picture state amplitudes evolve in accordance with Eq. (1b), where the proresonant coefficient matrix is given by

$$\mathbf{C}(\mathbf{t})=\frac{i}{2}E^0\begin{bmatrix} 0 & \mu_{12}\exp(-i\tilde{\omega}_{21}t) & \cdots & \mu_{1N}\exp(-i\tilde{\omega}_{N1}t) \\ \mu_{21}\exp(i\tilde{\omega}_{21}t) & 0 & \cdots & \mu_{2N}\exp(-i\tilde{\omega}_{N2}t) \\ \vdots & \vdots & & \vdots \\ \mu_{N1}\exp(i\tilde{\omega}_{N1}t) & \mu_{N2}\exp(i\tilde{\omega}_{N2}t) & \cdots & 0 \end{bmatrix} . \tag{27}$$

The reason for selecting only the proresonant part of the total Hamiltonian operator will become clear from what follows. In Eq. (27), $\tilde{\omega}_{kl}=\omega_{kl}-\omega$ is the detuning frequency from the level separation $\omega_{kl}=\omega_k-\omega_l$, where the eigenstate $|\,k\,\rangle$ has energy ω_k, and $\mu_{kl}=\langle k\,|\mu_z\,|\,l\,\rangle$ is the dipole transition matrix element coupling the states $|\,k\,\rangle$ and $|\,l\,\rangle$, μ_z being the z component of the dipole moment operator. There are a number of implicit assumptions in Eq. (27). First, the states $|\,k\,\rangle$ are of definite parity and hence the absence of diagonal entries in $\mathbf{C}(t)$ since $\langle k\,|\mu_z\,|\,k\,\rangle=0$ for an isolated freely rotating system. Second, the RWA demands that $\omega\sim\omega_{kl}$ and $|\,\mu_{kl}E^0\,|\ll 2\omega$ for all $k,l=1,2,\ldots,N$; while the second condition can be met by having a weak field strength and/or a sufficiently small transition moment as dictated by the prevailing selection rules, the first condition is generally valid only for the fundamental $\omega\sim\omega_{21}$. This essentially sets an upper limit on the number of levels $N-2$ to be included in any discussion of the interaction of the field $E(t)$ in near resonance with ω_{21}.

If Eq. (27) is substituted into (26) one obtains

$$\begin{aligned} &\sum_{j=1}^{N}(a_{jk}\mu_{kj}-a_{kj}\mu_{jk})=0, \quad k=1,2,\ldots,N \ , \\ &\sum_{j=1}^{N}(a_{kj}\mu_{jl}-a_{jl}\mu_{kj})=-i\tilde{\omega}_{kl}\mu_{kl}, \quad k>l=1,2,\ldots,N \ , \\ &\sum_{j=1}^{N}(a_{kj}\mu_{jl}-a_{jl}\mu_{kj})=-i\tilde{\omega}_{lk}\mu_{kl}, \quad l>k=1,2,\ldots,N \ . \end{aligned} \tag{28a}$$

The compatibility condition and general solution of the linear system in Eq. (28a) are known[8(c)]. However, here we eschew this line of inquiry in favor of examining the consequences of assuming **A** to be diagonal. With $a_{ij}=\delta_{ij}a_{ii}$, Eq. (28a) reduces to

$$a_{kk}=a_{ll}+i\tilde{\omega}_{kl}, \quad k>l=1,2,\ldots,N\ , \tag{28b}$$

whereupon the system in Eq. (26) is now overdetermined since it represents $N(N-1)/2$ equations in N unknowns. Even a_{11} is arbitrary. In the case of a three-level system, for example, $a_{33}=a_{11}+i\tilde{\omega}_{31}$ or $a_{11}+i(\tilde{\omega}_{31}-\omega)$ according to Eq. (28b). This ambiguity can be lifted by redefining the proresonant $\mathbf{C}(t)$ to exclude the μ_{13} coupling, say, but to include both the μ_{12} and μ_{23} couplings; if $|1\rangle$ and $|3\rangle$ are of like parity but $|2\rangle$ is of opposite parity then the ambiguity is automatically removed since μ_{13} vanishes whereas μ_{12} and μ_{23} are nonzero. This strategy is inherent in Freed's applications of the PFT scheme[7] to double- and triple-resonance interactions of few-level systems. There are two additional approaches to the determination of the diagonal matrix **A**. In the first approach Eq. (28b) is restricted to the serial generation of the a_{kk}'s through the $N-1$ relations

$$a_{kk}=a_{k-1k-1}+i\tilde{\omega}_{kk-1}, \quad k=2,\ldots,N \tag{28c}$$

and the missing relation results in a_{11} being arbitrary, say, $a_{11}=0$. This approach is justified if in the proresonant $\mathbf{C}(t)$ only the bidiagonal entries are retained, i.e., $\mu_{ij}=0$ if $|i-j|>1$. In the second approach the a_{kk}'s are taken for $k=2,\ldots,N$ as

$$a_{kk}=i(\omega_{kl}-m_k\omega)\ , \tag{28d}$$

where m_k is an integer such that $|a_{kk}|<\omega/2$, starting with $a_{11}=0$. The corresponding entries retained in $\mathbf{C}(t)$ involve μ_{jk} which is taken to be nonzero when $|m_j-m_k|\neq 1$; in this way one incorporates into the proresonant Hamiltonian operator only the most nearly resonant multiphoton transitions from the ground state to all other states. With both of these approaches the entries in **A** are obtained on the basis of the near resonance of the field with pairs of coupled states $|k\rangle$ and $|l\rangle$ and without appeal to the magnitude of the coupling strength $|E^0\mu_{kl}|$ relative to the laser frequency $\omega\sim\omega_{kl}$. This latter feature originates with the decoupling of the dependence of the a's on the resonance off-sets $\tilde{\omega}$'s *and* the dipole transition matrix elements μ's, as expressed in Eq. (28a), when one assumes **A** to be diagonal. When $\omega=0$ and $E^0=E^s/2$ so that the N-level system is interacting with a static field of strength E^s, there is no ambiguity in determining the entries in a diagonal **A** through Eq. (28b) even without having to resort to the omission of system-field couplings in $\mathbf{C}(t)$. Both the QRA and the equivalent RFT procedures select nonzero entries in the proresonant matrix $\mathbf{C}(t)$ on the basis of Eqs. (28c) and (28d).

Thus, while Eq. (3) formally defines a reference frame in which the Hamiltonian operator is constant, the realization of **A** through Eq. (26) may require that the given Hamiltonian be simplified whether through appeal to the RWA, selection rules, neglect of unimportant couplings, etc.

B. CH excitation in CD$_3$H

Quack and Sutcliffe have considered[6(a)] the excitation of a truncated (to nine levels) anharmonic oscillator model of the CH strength in CD$_3$H within the QRA (or tridiagonal RFT) and for a range of intensities they compared computed time-resolved spectra at near- and off-resonant frequencies with those calculated within the Floquet approximation.[16] In this section we adopt this model to demonstrate the application of the Leverrier-Bateman resolvent scheme in evaluating the evolution operator given in Eq. (7) on the assumption that a suitable Kubo-type transformation matrix has been determined. The energies and transition moments for the truncated anharmonic oscillator model are as reported by Quack and Sutcliffe.

In selecting the Kubo-type transformation matrix we applied Eq. (28a), assuming **A** to be diagonal. At laser frequencies below about 2750 cm^{-1} only first subdiagonal transition matrix elements are included whereas at higher frequencies one also incorporates coupling between the uppermost energy levels by the inclusion of matrix elements that belong to the second subdiagonals of the dipole transition matrix. Neglect of other couplings, in addition to the RWA, amounts to a simplification of the Hamiltonian operator of the system such that one can determine a diagonal Kubo-type transformation matrix **A** and hence the evolution operator through Eq. (7). As previously mentioned, this choice of **A** is independent of the laser field strength. When $\omega=0$ as in a static electric field, the complete transition matrix is retained and the diagonal entries of **A** are given by Eq. (28b). With **A** diagonal, $N_{kr,l}=\delta_{rk}\delta_{lk}$ and for the most interesting case wherein the ground state is initially fully populated so that $c_s(0)=\delta_{s1}$, the time-resolved transition probability $P_{kk}(t)$ given in Eq. (21a) reduces to

$$P_{kk}(t)=\exp[2\,\mathrm{Re}(\lambda_k)t]\left|\sum_{m=1}^{N}\exp(\tilde{\lambda}_m t)\tilde{N}_{k1,m}\right|^2\ , \tag{29a}$$

while the Laplace time-averaged transition probability P_{kk}^{τ} given in Eq. (21b) reduces to

$$P_{kk}^{\tau}=\sum_{m,m'=1}^{N}\tilde{N}_{k1,m}\tilde{N}_{k1,m'}^{*}/\{1-\tau[2\,\mathrm{Re}(\lambda_k)+\tilde{\lambda}_m+\tilde{\lambda}_{m'}^{*}]\}\ . \tag{29b}$$

The decay rate of the uppermost level $|N\rangle$, whose energy is complex $(\omega_N-i\gamma_n/2)$ by ascribing to it the phenomenological radiative width γ_N, is $\gamma_N P_{NN}(t)$, whence from Eq. (29),

$$P_{\mathrm{diss}}(t)=\gamma_N \sum_{m,m'=1}^{N} \widetilde{N}_{N1,m}\widetilde{N}^{\,*}_{N1,m'}(\exp\{[2\,\mathrm{Re}(\lambda_N)+\widetilde{\lambda}_m+\widetilde{\lambda}^{\,*}_{m'}]t\}-1)/[2\,\mathrm{Re}(\lambda_n)+\widetilde{\lambda}_m+\widetilde{\lambda}^{\,*}_{m'}] \tag{30a}$$

and

$$P^{\tau}_{\mathrm{diss}}=\tau\gamma_N \sum_{m,m'=1}^{N} \widetilde{N}_{N1,m}\widetilde{N}^{\,*}_{N1,m'}/\{1-\tau[\,2\,\mathrm{Re}(\lambda_N)+\widetilde{\lambda}_m+\widetilde{\lambda}^{\,*}_{m'}]\} \tag{30b}$$

represent the time-resolved and Laplace time-averaged dissociation probabilities, respectively. From Eqs. (29b) and (30b) it follows that $P^{\tau}_{\mathrm{diss}}=\tau\gamma_N P_{NN}$. The instantaneous average energy absorbed by the system is

$$\langle E \rangle = \sum_{k=1}^{N} \omega_k P_{kk}(t)+\omega_N P_{\mathrm{diss}}(t)\ , \tag{31a}$$

while its Laplace time-averaged analogue is

$$\langle E \rangle_\tau = \sum_{k=1}^{N} \omega_k P^{\tau}_{kk}+\omega_N P^{\tau}_{\mathrm{diss}}\ . \tag{31b}$$

Two comments are in order with respect to Eq. (30). First, since $P_{\mathrm{diss}}(t)=1-\sum_{k=1}^{N} P_{kk}(t)$ then $P_{\mathrm{diss}}(\infty)=1$ as $\sum_{k=1}^{N} P_{kk}(\infty)=0$ if there is leakage of population at a finite rate through the uppermost level. Second, Eq. (30b) is valid for $\tau \ll \gamma_N^{-1}$ and of course $P^{\tau}_{\mathrm{diss}}=0$ if $\gamma_N=0$ since then there is no leakage of population out of the N-level system.

To evaluate P_{kk} or P_{diss} requires the eigenvalues of $\mathbf{A}$ and of $\mathbf{C}(0)-\mathbf{A}$, where $\mathbf{C}(0)$ is the coefficient matrix in Eq. (27) evaluated at $t=0$ but with the neglect of all dipole transition matrix elements other than those required to define the diagonal matrix $\mathbf{A}$. Using this simplified version of $\mathbf{C}(0)$ one evaluates the $\mathbf{Z}_i$'s through the Leverrier algorithm given in Eqs. (20b) and (20c) and hence the Bateman coefficient matrices through Eq. (20a) or (23b). For the particular application considered here $\mathbf{C}(0)-\mathbf{A}$ has no degenerate eigenvalues. The performance of the Leverrier-Bateman method was assessed through Eqs. (24) and (25); generally these conditions were fulfilled to within machine precision (for a 32-bit word, typically 2^{-26} in single and 2^{-59} in double) at least.

As a check on the code used here, the time-resolved transition probabilities were calculated using both the Leverrier-Bateman resolvent method and a complete spectral decomposition scheme to evaluate $\exp[(\mathbf{C}(0)-\mathbf{A})t]$. The latter involves computing $\exp[(\mathbf{C}(0)-\mathbf{A})t]$ as $\mathbf{Z}\exp(\mathbf{\Lambda}t)\mathbf{Z}^{-1}$, where $\mathbf{\Lambda}$ is the diagonal matrix containing the eigenvalues of $\mathbf{C}(0)-\mathbf{A}$, and $\mathbf{Z}$ has the corresponding eigenvectors as columns. The computation time required to evaluate the Bateman matrices $\widetilde{\mathbf{N}}_k=(\widetilde{N}_{ij,k})$ for $k=1,2,\ldots,N$ is significantly shorter than that required to evaluate $\mathbf{Z}=(z_{ij})$ *and* $\mathbf{Z}^{-1}=(\widetilde{z}_{ij})$, the evaluation of $\mathbf{\Lambda}$ being a task common to both approaches. The matrix elements of $\widetilde{\mathbf{N}}_k$ are related to those of $\mathbf{Z}$ and $\mathbf{Z}^{-1}$ by $\widetilde{N}_{ij,k}=z_{ik}\widetilde{z}_{kj}$. Clearly evaluation of the independent $k=1,2\ldots,N$ Bateman matrices $\widetilde{\mathbf{N}}_k$ can be efficiently executed by parallel array processors. We go beyond Quack's and Sutcliffe's[6(a)] model calculations on the CH Morse oscillator by computing frequency sweep spectra with the inclusion of uniform relaxation, as well as time-resolved transition probabilities and dissociation probabilities in the presence of an oscillating or a static electric field.

Figure 1 displays the time-averaged transition probabilities for the first three levels of the CH anharmonic oscillator over the frequency range 2910–2990 cm^{-1} at a field intensity of 100 GW cm^{-2} and assuming a uniform relax-

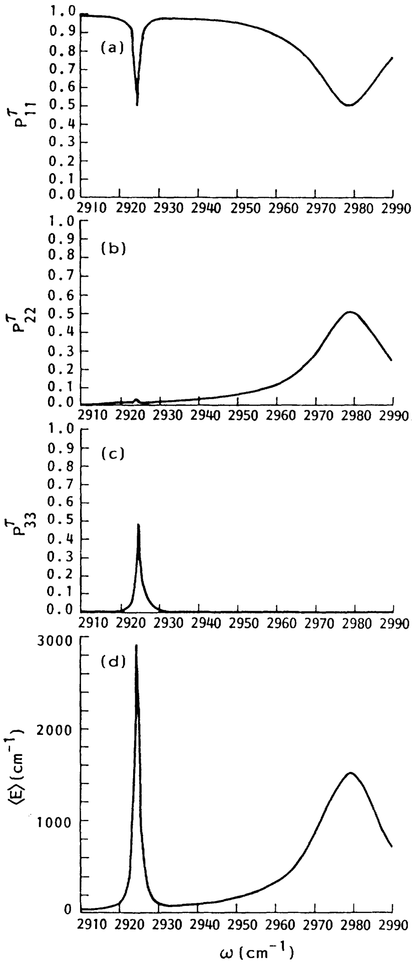

FIG. 1. The transition probability P^{τ}_{kk} with (a) $k=1$, (b) $k=2$, and (c) $k=3$ for the CH anharmonic oscillator excitation at a laser field intensity of 100 GW cm^{-2} over the frequency range 2910–2990 cm^{-1}, and with a relaxation time of 1 ns. The average energy $\langle E \rangle$ absorbed by the system, which was initially in the ground state, is displayed in (d).

ation time of 1 ns. The one-photon resonance occurs at $\omega \sim 2979.2$ cm^{-1} and results in the near saturation of the ground and first excited states of the system. The uniform relaxation time is long enough for the spectrum in Fig. 1 to exhibit the two-photon resonance at $\omega \sim 2924.6$ cm^{-1}, which results in the saturation of the ground and second excited state of the system. Also displayed in Fig. 1 is the average energy absorbed by the CH anharmonic oscillator, the amount of energy absorbed reflecting both the saturation of the system and the photon multiplicity of the resonance. The time-resolved transition probabilities at the one- and two-photon resonance frequencies are shown in Fig. 2 as well as the instantaneous average energies absorbed. It is perhaps worthwhile mentioning that only[15(b)] if the simplified version of $\mathbf{C}(t)$ remains periodic in time will $P_{kk}(t)$ be almost periodic. Retaining all dipole couplings in $\mathbf{C}(t)$ does not cause much population leakage from the system in the presence of a static electric field of strength 1.39×10^8 V cm^{-1} as evident from Fig. 3 where the time-resolved transition probability for the first excited state and the average energy absorbed by the system are displayed. In contrast, we show in Fig. 4 the dissociation probabilities for the system in the absence of uniform relaxation, assuming a radiative width of 2×10^{11} s^{-1} for the uppermost level, in a laser field of frequency 2900 cm^{-1} and of strength 2.17×10^9 V cm^{-1} and in a static electric field of the same strength. Clearly the time scales over which $P_{\text{diss}}(t)$ approaches unity are vastly different with the laser field being more effective in depleting the population within the truncated anharmonic oscillator.

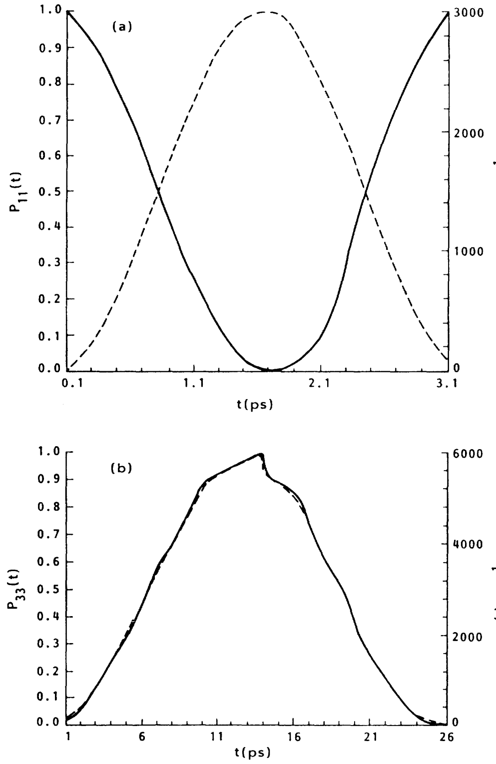

FIG. 2. The time-resolved transition probability $P_{kk}(t)$ (——, left ordinate) and the average energy absorbed $\langle E \rangle$ (— — —, right ordinate) by the CH anharmonic oscillator at (a) the one-photon resonance frequency 2979.2 cm^{-1}, and at (b) the two-photon resonance frequency 2924.6 cm^{-1} in a laser field of intensity 100 GW cm^{-2}.

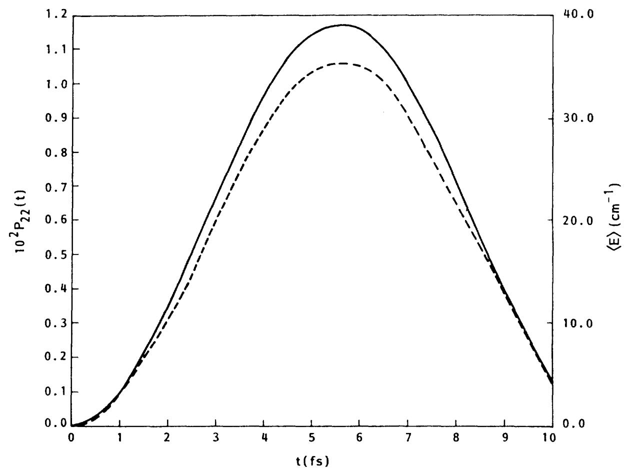

FIG. 3. The time-resolved transition probability $P_{22}(t)$ (——, left ordinate) and the average energy absorbed $\langle E \rangle$ (— — —, right ordinate) by the CH anharmonic oscillator in a static field of strength 1.39×10^8 V cm^{-1}.

IV. SUMMARY AND CONCLUSIONS

In this paper we have derived Eq. (7) as the form of the evolution operator $U(t)$ governing the time development of the state amplitudes of a quantized system in accordance with Eq. (1b), predicted on the assumption that the evolution of the Hamiltonian operator $H(t)$ of the system is described by Eq. (10) in terms of a time-independent Kubo-type operator A defined in Eq. (2). If $H(t)$ is Hermitian then an anti-Hermitian A assures the unitarity of $U(t)$. We have not provided existence criteria for A.

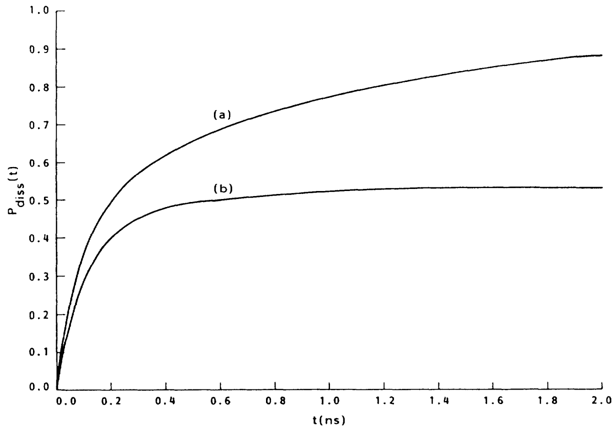

FIG. 4. The time-resolved dissociation probability $P_{\text{diss}}(t)$ for the CH anharmonic oscillator whose uppermost level has a radiative width 2×10^{11} s^{-1} in (a) a laser field of strength 2.17×10^9 V cm^{-1} and frequency 2900 cm^{-1}, and in (b) a static field of strength 2.17×10^9 V cm^{-1}.

Indeed even if A exists it is not necessarily unique; since we can formally eliminate the explicit dependence of $U(t)$ on A through Eq. (8), the density matrix $\rho(t) = U(t)\rho(0)U^{\dagger}(t)$ is independent of the particular choice of A. Further, we do not claim the existence of A to be universally true for a general quantized system.

However, in the context of an N-level system dipole interacting with a cw laser, we showed how $\mathbf{A}$ may be systematically constructed through an algebraic algorithm given in Eq. (26). The solution of Eq. (26) requires the introduction of certain simplifications in $\mathbf{H}(t)$, specifically the appeal to the RWA, whereupon Eq. (26) reduces to (28a). In pursuing the additional assumption that $\mathbf{A}$ is diagonal, two interesting outcomes emerge. First, the overdeterminism in Eq. (28b) requires one to invoke the relevant transition dipole selection rules in order to validate the neglect of unimportant couplings, as in Freed's application[7] of the PFT, or through the retention of only the most nearly resonant multiphoton transitions from the ground state to all other states, as in Quack's application[6] of the QRA or Whaley's and Light's application[5] of the RFT. Second, the matrix elements of $\mathbf{A}$ depend only on the resonance off-sets and are independent of the relative coupling strength matrix elements. This latter feature contrasts with Tietz's and Chu's most probable path approximation[17(a)] and Chang's and Wyatt's artificial intelligence techniques[17(b),17(c)] for pruning the order of the Floquet matrix;[16] these approaches employ selection criteria which are dependent upon both resonance detunings and coupling strengths. The Kubo transformation yields a sparse time-independent Hamiltonian without any reduction in its order. Pursuit of the solution of Eq. (28a) for a general Kubo-type transformation in an attempt to retain a dependency on coupling strength parameters proves to be futile. In fact it is generally true that the system in Eq. (28a) is incompatible[8(c)] so that the assumption that $\mathbf{A}$ is diagonal was a necessary expedient.

Having determined a suitable Kubo-type transformation matrix for a specific application, one must then grapple with the construction of the matrix exponentials appearing in Eq. (7). In this paper we have proposed the use of the Leverrier-Bateman resolvent method which is one among what an authoritative review[18] described as "nineteen dubious ways to compute the exponential of a matrix"; on consideration of computational stability and efficiency, some of these methods were deemed to be preferable to others, but none were judged to be entirely satisfactory. Although computationally laborious, the resolvent method is insensitive to the vagaries of $\mathbf{C}(0) - \mathbf{A}$. The method does not require the eigenvectors corresponding to the eigenvalues, a feature in common with the recursive residue generation method promoted by Wyatt and co-workers[19] for the evaluation of transition amplitudes of systems with a large ($\geq 10^3$) number of levels. The sum rule given in Eq. (23a) for the generalized Bateman matrices or its simplified version given in Eq. (24a), as well as the projection and idempotent properties of the Bateman matrices given in Eqs. (24b) and (24c), in addition to the condition given in Eq. (25), serve to gauge the numerical performance of the method. The generalizations of Eqs. (19) and (24a), given in Eqs. (17) and (23a), respectively, are new, as far as this author is aware. We illustrated the application of the method by considering the excitation of the CH stretch in CD_3H.

The Leverrier-Bateman resolvent method is equally applicable to the evaluation of the matrix exponentials appearing in the Riemann product integral representation[20] of $\mathbf{U}(t)$ for multilevel systems interacting with sinusoidal or nonsinusoidal fields. As pointed out recently by Hirschfelder,[21] the evolution operators on the serial time intervals can be determined *en bloc* by parallel array processors as can their requisite Bateman matrices.

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[1] V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov, and E. A. Ryabov, *Multiple Photon Infrared Laser Photophysics and Photochemistry* (Harwood, New York, 1985).

[2] (a) F. J. Dyson, Phys. Rev. **75**, 1736 (1949); (b) C. C. Lam and P. C. W. Fung, Phys. Rev. A **27**, 1760 (1983).

[3] P. Pechukas and J. C. Light, J. Chem. Phys. **44**, 3897 (1966).

[4] T. M. Einwohner, J. Wong, and J. C. Garrison, Phys. Rev. A **14**, 1452 (1976).

[5] K. B. Whaley and J. C. Light, Phys. Rev. A **29**, 1188 (1984).

[6] (a) M. Quack and E. Sutcliffe, J. Chem. Phys. **83**, 3805 (1985); (b) M. Quack, *ibid.* **69**, 1282 (1978).

[7] K. Freed, J. Chem. Phys. **43**, 1113 (1965).

[8] (a) R. Kubo, in *Lectures in Theoretical Physics,* edited by W. E. Brittin and L. G. Dunham (Interscience, New York, 1959), Vol. I, p. 120; (b) G. Fano, *Mathematical Methods of Quantum Mechanics* (McGraw-Hill, New York, 1971); (c) G. E. Shilov, *Linear Algebra* (Dover, New York, 1977).

[9] R. M. Wilcox, J. Math. Phys. **8**, 962 (1967), and the source references therein.

[10] R. D. Richtmyer and S. Greenspan, Commun. Pure Appl. Math. **18**, 107 (1965).

[11] (a) R. A. Frazer, W. J. Duncan, and A. R. Collar, *Elementary Matrices* (Cambridge University, Cambridge, 1960); (b) N. J. Pullman, *Matrix Theory and its Applications* (Dekker, New York, 1976).

[12] (a) U. J. J. Leverrier, J. Math. **5**, 230 (1840); (b) V. N. Faddeeva, *Computational Methods of Linear Algebra* (Dover, New York, 1959).

[13] H. Bateman, Proc. Cambridge Philos. Soc. **15**, 423 (1910).

[14] (a) *IMSL Library Reference Manual* (IMSL Inc., Houston, 1982), 9th ed., (b) B. T. Smith, J. M. Boyle, J. J. Dongarra, B. S. Garbow, Y. Ikebe, U. C. Klema, and C. B. Moler, *Matrix Eigensystem Routines-EISPACK Guide* (Springer, Berlin, 1976).

[15] (a) A. S. Besicovitch, *Almost Periodic Functions* (Dover, New York, 1954); (b) T. Hogg and B. A. Huberman, Phys. Rev. A **28**, 22 (1983).

[16] S.-I. Chu, Adv. At. Mol. Phys. **21**, 197 (1985).

[17] (a) J. V. Tietz and S.-I. Chu, Chem. Phys. Lett. **101**, 446 (1983); (b) J. Chang and R. E. Wyatt, *ibid.* **121**, 307 (1985); (c) J. Chem. Phys. **85**, 1826 (1986).

[18] C. Moler and C. van Loan, SIAM Rev. **20**, 801 (1978).

[19] (a) A. Nauts and R. E. Wyatt, Phys. Rev. Lett. **51**, 2238 (1983); (b) Phys. Rev. A **30**, 872 (1984); (c) I. Schek and R. E. Wyatt, J. Chem. Phys. **83**, 3028 (1985).

[20] (a) G. F. Thomas and W. J. Meath, J. Phys. B **16**, 951 (1983); (b) G. F. Thomas, Phys. Rev. A **32**, 1515 (1985).

[21] J. O. Hirschfelder, Int. J. Quantum Chem. **29**, 1139 (1986).