

New Approach to Many-State Quantum Dynamics: The Recursive-Residue-Generation Method

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A new computational approach to time-dependent transition amplitudes in multistate quantum systems is developed. The method, which avoids explicit computation of matrix eigenvectors, is based upon the recursive generation of residues of Green's functions. The residues are computed from the eigenvalues of several tridiagonal matrices. Numerical results are presented for multiphoton excitation of overtones in a system with over 3000 states.

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Over the past few years, remarkable insight has been gained from the theoretical study of time-evolving quantal systems. These studies include the dephasing of initial zero-order states in conservative systems¹ and the preparation and evolution of excited states through coupling of the system to an external driving field.² Typically these studies involve fewer than several hundred coupled states, although studies involving about 10^3 states are amenable with a CRA Y-level computer.³ This severe limitation arises from the necessity of computing and storing all (or many) of the eigenvectors of the Hamiltonian (or evolution operator). However, most time-evolving systems (molecules, surfaces, solids) involve large numbers of strongly coupled states and are thus currently inaccessible to "exact" quantum dynamical studies.

During the past decade, the situation with regard to static or time-averaged properties has changed as a result of the development and utilization of new theoretical techniques. Among these, recursion methods are prominent. For example, the Cambridge solid-state physics group has developed a recursive approach to the calculation of local state (electronic or vibrational) densities in disordered solids.⁴ Similar techniques are being used in other areas.⁵⁻⁷ In some cases, depending upon the extent of coupling among the states, systems involving from 10^4 to 10^5 states are being studied.

In this Letter, recursion methods are extended to the calculation of time-dependent transition amplitudes, with particular emphasis upon multiphoton excitation in laser-driven molecules. The recursion method is particularly adept at handling problems with very large, but sparse, coupling matrices. In contrast to matrix diagonalization methods, this recursion method focuses upon individual transition amplitudes—those leading to probabilities probed in an experiment. The method is based upon the recursive generation

and refinement of residues of several Green's functions. A novel feature is that the residues are computed from *sets* of eigenvalues—*explicit construction of eigenvectors is not required*. Once the residues are known with sufficient accuracy (the calculation can be terminated at various levels of approximation), time-dependent transition probabilities are easily computed.

The transition amplitude, for a system described by a time-independent Hamiltonian H (denoted later as M for laser-molecule interactions), between an initial state $|i\rangle$ (at $t_0=0$) and a final state $|f\rangle$ (at time t) is given by⁸

$$\langle f|U(t|0)|i\rangle = \langle f|\exp(-iHt)|i\rangle. \quad (1)$$

If $|i\rangle$ and $|f\rangle$ belong to the spectrum of a time-independent Hamiltonian H^0 , then transition between these states is regarded as being induced by the (time-independent) perturbation $V = H - H^0$, which makes the system "unstable." Let us write the eigenvalue equation for H as $H|\alpha\rangle = \epsilon_\alpha|\alpha\rangle$, $\alpha = 1, 2, \dots$. A discrete nondegenerate spectrum is assumed, together with the usual completeness and orthonormality relations: $\sum |\alpha\rangle\langle\alpha| = 1$; $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$. From Eq. (1), we obtain

$$\langle f|U(t|0)|i\rangle = \sum_\alpha \langle f|\alpha\rangle\langle\alpha|i\rangle \exp(-i\epsilon_\alpha t). \quad (2)$$

For a relatively small basis of N states ($N \leq 10^3$), the standard way to compute transition amplitudes is to diagonalize the matrix H to obtain all eigenvalues and eigenvectors. However, this approach is intractable for larger bases.

The purpose of this Letter is to show that time-dependent transition amplitudes can be readily computed, for large bases ($N \gg 10^3$), *without resorting to explicit knowledge of the eigenstates $|\alpha\rangle$* . This method is based upon recursive generation of the residues of Green's functions; we term this the *recursive-residue-generation method* (RRGM).

The RRG M is based upon the following ideas.

(i) When $\langle f|\alpha\rangle$ and $\langle i|\alpha\rangle$ are real valued,⁹ it is

easy to check that the transition amplitude $i \rightarrow \alpha$ $-f$ is given by the difference of two positive numbers,¹⁰

$$\langle f | \alpha \rangle \langle \alpha | i \rangle = \frac{1}{2} [\langle u_0 | \alpha \rangle^2 - \langle v_0 | \alpha \rangle^2], \quad (3)$$

where two *transition vectors* are now associated with each pair (i, f) :

$$|u_0\rangle = 2^{-1/2}(|i\rangle + |f\rangle), \quad |v_0\rangle = 2^{-1/2}(|i\rangle - |f\rangle).$$

(ii) $\langle u_0 | \alpha \rangle^2$ is the residue $R_u(\alpha)$ corresponding to the simple pole ϵ_α of the Green's function

$$G_u(z) = \langle u_0 | (z\mathbb{1} - H)^{-1} | u_0 \rangle = \sum \langle u_0 | \alpha \rangle^2 / (z - \epsilon_\alpha),$$

where z does not belong to the spectrum of H . The transition amplitude in Eq. (2) can then be written

$$\langle f | U(t|0) | i \rangle = \sum_\alpha R_{if}(\alpha) \exp(-i\epsilon_\alpha t), \quad (4)$$

where $R_{if}(\alpha) = [R_u(\alpha) - R_v(\alpha)]/2$.

(iii) The residue $R_u(\alpha)$ is, by its very definition,¹¹

$$R_u(\alpha) = \lim_{z \rightarrow \epsilon_\alpha} [(z - \epsilon_\alpha) G_u(z)], \quad (5)$$

$$R_u(\alpha) = \Gamma_{1,1}^{(\alpha)}(u) \Gamma_{2,2}^{(\alpha)}(u) \cdots \Gamma_{\alpha-1,\alpha-1}^{(\alpha)}(u) \Gamma_{\alpha,\alpha+1}^{(\alpha)}(u) \cdots \Gamma_{N-1,N}^{(\alpha)}(u), \quad (7)$$

where $\Gamma_{\beta,\gamma}^{(\alpha)}(u) = (\epsilon_\alpha - \epsilon_\beta^{(u)}) / (\epsilon_\alpha - \epsilon_\gamma)$. The significant result is that *residues, and hence transition amplitudes, can be computed directly from three sets of eigenvalues* $[\{\epsilon_\alpha\}]$ and $\{\epsilon_\alpha^{(u)}\}$ from the $\{|u_n\rangle\}$ basis and $\{\epsilon_\alpha(v)\}$ from the $\{|v_n\rangle\}$ basis], *without explicitly constructing eigenvectors.*

In order to generate these sets of eigenvalues, H is converted to a Jacobi (tridiagonal) matrix J by the Lanczos recursion method.^{12,13} Let a_n and b_{n+1} ($n = 0, 1, 2, \dots, N-1$) denote diagonal and off-diagonal elements in row $(n+1)$ of J ; this self-energy and nearest-neighbor coupling energy define a link in the one-dimensional chain (a 1D disordered lattice) used to portray J . In the recursion scheme, each additional step "forges a new link in the chain." Given the recursion vectors $|n-1\rangle$ and $|n\rangle$ in fast storage, the next vector, self-energy, and coupling energy are formed by the three-term explicit recurrence relation

$$|n+1\rangle b_{n+1} = H|n\rangle - |n\rangle a_n - |n-1\rangle b_n, \quad (8)$$

where $a_n = \langle n | H | n \rangle$, $b_n = \langle n | H | n-1 \rangle = \langle n-1 | H | n \rangle$, and where b_{n+1} is chosen to normalize $|n+1\rangle$. The starter is $|1\rangle b_1 = H|0\rangle - |0\rangle a_0$, with $|0\rangle = |u_0\rangle$ or $|0\rangle = |v_0\rangle$. Once we have N_c chain links, the eigenvalues $\{\epsilon_\alpha\}$ of J are easily (10% more central processor time and no additional storage) generated (TQLRAT from the EISPACK library is used). Then setting the coupling term in the first

so that $R_{if}(\alpha)$ can be computed if we know both $G_u(z)$ and $G_v(z)$.

(iv) Focusing upon $G_u(z)$, imagine the construction of a new orthonormal basis (from the original H^0 basis), in which $|u_0\rangle$ is the first member. In the $\{|u_n\rangle, n = 0, 1, \dots, N-1\}$ basis, we need only the $(1, 1)$ matrix element of the resolvent $(z\mathbb{1} - H)^{-1}$ in order to construct $G_u(z)$. By the rule to invert matrices,

$$G_u(z) = \frac{\det[z\mathbb{1} - H]_r}{\det[z\mathbb{1} - H]} = \prod_{\alpha=1}^{N-1} (z - \epsilon_\alpha^{(u)}) / \prod_{\alpha=1}^N (z - \epsilon_\alpha), \quad (6)$$

where $[z\mathbb{1} - H]_r$ is the *reduced matrix* obtained by deleting the first row and column from $[z\mathbb{1} - H]$. The eigenvalues of H and H_r are $\{\epsilon_\alpha\}$ and $\{\epsilon_\alpha^{(u)}\}$, respectively.

(v) From Eqs. (5) and (6), the residue is then the product of $N-1$ factors (each typically the order of unity):

chain link (b_1) equal to zero and re-diagonalizing matrix J generates the second set of eigenvalues $\{\epsilon_\alpha^{(u)}\}$. Since each recursion step generates a more distant environment of the transition of interest, the method usually converges for $N_c \ll N$; most of the physics of the $i \rightarrow f$ transition is concentrated in a relatively small subspace of the full Hilbert space.¹⁴

As recursion proceeds, loss of significant figures in finite precision arithmetic leads to a gradual (after 30-50 steps) loss of global orthogonality in the $\{|u_n\rangle\}$ basis. As a result, multiple copies ("ghosts") of some eigenvalues are produced, and some "incorrect eigenvalues" (which settle onto eigenvalues as N_c increases) may also be generated. These "bad" eigenvalues must be removed before computing residues from Eq. (7). This is done in a two-step procedure. First, all multiple copies of the N_c eigenvalues ϵ_α and the $N_c - 1$ eigenvalues $\epsilon_\alpha^{(u)}$ are deleted. Second, the two lists of eigenvalues are compared to make sure that they form a Sturm sequence¹⁵; we should have $\epsilon_\alpha < \epsilon_\alpha^{(u)} < \epsilon_{\alpha+1} < \epsilon_{\alpha+1}^{(u)}$. However, if a near degeneracy is uncovered, $|\epsilon_{\alpha+1} - \epsilon_\alpha^{(u)}| < \delta$ (usually we set $\delta = 10^{-5}$), then $\epsilon_{\alpha+1}$ and $\epsilon_\alpha^{(u)}$ are both deleted from their respective lists. This algorithm was always successful for model problems related to the Hamiltonian in

Eq. (12). Symptoms of failure to update the eigenvalue lists correctly are (1) a residue greater than unity is produced, and/or (2) the sum of the residues deviates from unity (the residues normally add to 1.0 to within about 10^{-10}). Although selective periodic reorthogonalization¹⁶ would eliminate these problems in the eigenvalue lists, it seems simpler to let the pathology develop and then apply this remedy.¹⁷

Now consider a quantum system driven by a classical monochromatic field, $E^0 \cos(\omega t)$. It is a consequence of Floquet's theorem^{18,19} that the propagator is the product of a periodic unitary operator times the exponential of a Hermitian

time-independent operator,

$$U(t|0) = P(t|0) \exp(-iMt), \quad (9)$$

where $P(t+\tau|0) = P(t|0)$, in which the optical period is $\tau = 2\pi/\omega$, and $P(0|0) = I$. For time intervals which are integer multiples of the optical period, the transition amplitude takes the form of Eq. (2), in which ϵ_α is the quasienergy associated with Floquet state $|\alpha\rangle$. In addition, M acts as an effective Hamiltonian in driving the system to the end of each optical cycle. M may be realized through¹⁹ the Magnus expansion²⁰ from the field-free Hamiltonian H^0 and the dipole coupling operator $V_{\text{rad}} = \mu E^0$,

$$\exp(-iM\tau) = \exp\left\{-i \int_0^\tau H(t) dt + \frac{1}{2} \int_0^\tau dt' \int_0^{t'} dt [H(t), H(t')] + \dots\right\}, \quad (10)$$

where $H(t) = H^0 + V_{\text{rad}} \cos(\omega t)$. Through third order in V_{rad} ,

$$M = H^0 - \omega^{-2} \left\{ [H^0, [H^0, V_{\text{rad}}]] - \frac{1}{4} [V_{\text{rad}}, [H^0, V_{\text{rad}}]] \right\}. \quad (11)$$

As a particular model, consider an anharmonic oscillator, dipole coupled to the laser, which is also linearly coupled to a multimode harmonic bath,

$$H^0 = A(a^\dagger a) + B(a^\dagger a)^2 + \sum_{j=1}^{N_b} \omega_j b_j^\dagger b_j + \sum_{j=1}^{N_b} V_{\text{int}}^{(j)} (a^\dagger b_j + a b_j^\dagger), \quad (12)$$

where a^\dagger, a and b_j^\dagger, b_j are boson raising and lowering operators for the pump mode²¹ and the j th bath mode, respectively. The last term in Eq. (12) provides for one-quantum exchange between the pump mode and each bath mode. In converting H^0 and V_{rad} into M , we retained only the lowest order in V_{rad} . If there are p states available in each of the $N_b + 1$ modes, then the total basis size is $N = p^{N_b+1}$. For the results reported here, $N_b = 4$ and $p = 5$, so that $N = 3125$. However, because of the simple form of the coupling terms in Eq. (12), only about 24 000 of the nearly 10^7 matrix elements in M are nonzero.

In Fig. 1, probabilities are shown for multiphoton excitation from the ground state to all pump-mode overtone states, $|0, 0, 0, 0, 0\rangle \rightarrow |f, 0, 0, 0, 0\rangle$ (the quantum numbers are for the pump mode, first bath mode, etc.), where $f = 1, \dots, 4$. In addition, the probability of surviving in the ground state is shown. These converged results were obtained by truncating the recursion at far fewer chain links than the full basis size (for $f = 0, 1, 2, 3$, and 4, the number of links used was $N_c = 100, 150, 150, 250$, and 1000). Total central processor time on a CYBER 170/750 was about 6 min. Similar results have been obtained for much larger bases involving nearly 15 000 states (of which there are about 1.4×10^5 nonzero

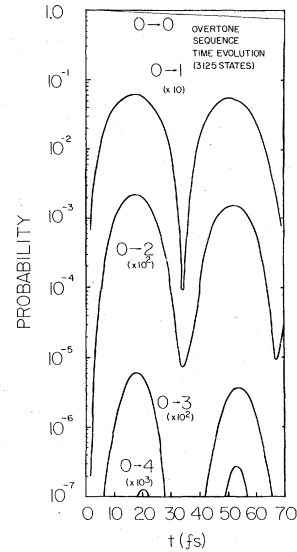


FIG. 1. Time-dependent transition probabilities $P_{if}(t)$, where $|i\rangle = |0, 0, 0, 0, 0\rangle$ is the ground state and $|f\rangle = |f, 0, 0, 0, 0\rangle$ is a pump-mode overtone state. There are 5 states per mode and 3125 states in the basis. The laser frequency is 1000 cm^{-1} . Parameters in inverse centimeters in the Hamiltonian in Eq. (12) are $A = 1000$, $B = -20$, $\omega_1 = 970$, $\omega_2 = 990$, $\omega_3 = 1010$, $\omega_4 = 1030$, $V_{\text{int}}^{(j)} = 30$ (independent of j), and $V_{\text{rad}} = 40$. States of the field-free Hamiltonian fall into bands separated by about 1000 cm^{-1} . The lowest band (1 state) lies near $E = 0 \text{ cm}^{-1}$, the first excited band (5 states) near 1000 cm^{-1} , etc.

matrix elements, out of a total of nearly 0.3×10^9). Further details are presented elsewhere.²² Applications are now possible to systems involving many more states than considered previously,²³ including the study of quantum chaos²⁴ and multiphoton excitation²⁵ in small polyatomic molecules.

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¹For example, see J. Brickman, in *Intramolecular Dynamics*, edited by J. Jortner and B. Pullman (Reidel, Dordrecht, 1982), p. 139; E. J. Heller and M. J. Davis, *J. Phys. Chem.* **86**, 2118 (1982); J. S. Hutchinson and R. E. Wyatt, *Phys. Rev. A* **23**, 1567 (1981).

²For example, see H. G. Galbraith and J. R. Ackers, in *Laser Induced Chemical Processes*, edited by J. I. Steinfeld (Plenum, New York, 1981), p. 1; C. D. Cantrell, V. S. Letokhov, and A. A. Makarov, in *Topics in Current Physics*, edited by M. S. Feld and V. S. Letokhov (Springer-Verlag, Heidelberg, 1980), Vol. 21, p. 165.

³D. P. Hodgkinson, A. J. Taylor, and A. G. Robiette, *J. Phys. B* **14**, 1803 (1981).

⁴R. Haydock, in *Excitations in Disordered Systems*, edited by R. Thorpe (Plenum, New York, 1981), p. 29, and *Comput. Phys. Commun.* **20**, 11 (1980), and *Solid State Phys.* **35**, 215 (1980).

⁵E. Haller, H. Köppel, L. S. Cederbaum, W. von Nies-

sen, and G. Bieri, *J. Chem. Phys.* **78**, 1359 (1983).

⁶M. C. M. O'Brien and S. N. Evangelou, *J. Phys. C* **13**, 611 (1980); J. R. Fletcher and D. R. Pooler, *J. Phys. C* **15**, 2695 (1982); S. Muramatsu and N. Sakamoto, *J. Phys. Soc. Jpn.* **46**, 1273 (1979).

⁷S. Alexander, A. Baram, and Z. Luz, *J. Chem. Phys.* **61**, 992 (1974).

⁸For example, M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), Chap. 8.

⁹A slight extension allows the treatment of complex amplitudes.

¹⁰See Haydock, third paper in Ref. 4, p. 250.

¹¹Z. Nehari, *Introduction to Complex Analysis* (Allyn and Bacon, Boston, 1961), p. 124.

¹²C. Lanczos, *J. Res. Natl. Bur. Stand.* **45**, 255 (1950).

¹³Our approach follows the discussion on pp. 222-231 in Haydock, third paper in Ref. 4.

¹⁴Also see Haydock, third paper in Ref. 4, pp. 230-232.

¹⁵R. J. Gault, R. F. Hoskins, J. A. Milner, and M. J. Pratt, *Computational Methods in Linear Algebra* (Wiley, New York, 1974), pp. 142-144.

¹⁶B. N. Parlett and D. S. Scott, *Math. Comput.* **33**, 217 (1979).

¹⁷Also see J. Cullum and R. A. Willoughby, *J. Comput. Phys.* **44**, 329 (1981), and IBM Research Report No. RC7456 (unpublished).

¹⁸J. H. Shirley, *Phys. Rev. B* **138**, 979 (1965); S. R. Barone, M. A. Narcowich, and F. J. Narcowich, *Phys. Rev. A* **15**, 1109 (1977).

¹⁹K. F. Milfeld and R. E. Wyatt, *Phys. Rev. A* **27**, 72 (1983).

²⁰P. Pechukas and J. C. Light, *J. Chem. Phys.* **44**, 3897 (1965).

²¹S. Leasure, *Chem. Phys.* **67**, 83 (1982).

²²A. Nauts and R. E. Wyatt, to be published.

²³Algebraic molecular Hamiltonians should be useful in this regard, since the nonzero matrix elements are easily computed and indexed. See R. D. Levine, *Chem. Phys. Lett.* **95**, 87 (1983), and references therein.

²⁴N. Moiseyev and R. E. Wyatt, to be published.

²⁵J. Chang, S. L. Ding, and R. E. Wyatt, to be published.