Natural expansion of vibrational wave functions: RRGM with residue algebra[a]

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The natural expansion (NE) of vibrational eigenstates is useful for identifying the optimum local coordinates for any vibrational energy and it provides a positive test for regular (nonstochastic) behavior. In previous NE analyses, both eigenvalues and eigenvectors of the Hamiltonian matrix were required. However, through use of the recursive residue generation method (RRGM), we will illustrate how to perform the NE analysis *without* the need to compute eigenvectors of the $N \times N$ Hamiltonian matrix. In addition, a new computational method to obtain all transition amplitudes among a set of states is developed. The method, based upon residue algebra, reduces the CPU requirement by a factor of $N/2$. To illustrate these procedures, the A_1 symmetry eigenfunctions in the classically chaotic regime (where the modes are strongly coupled) of a 2D model Hamiltonian are analyzed with the modified RRGM.

I. INTRODUCTION

The nonstatistical distribution of vibrational energy among molecular vibrational modes implies a localization of some of the energy in "privileged" modes. Such behavior can be observed even in the quasicontinuum if there exist eigenfunctions which are almost separable, for example, $\Psi \sim f(q_1)g(q_2)$ in the 2D case. Indeed, for several 2D model potentials,[1-3] numerical calculations have shown that there is still a "ladder" of equidistant eigenvalues having associated eigenfunctions which are almost separable, are localized, and can be assigned good quantum numbers.

The natural expansion (NE) method offers a systematic way to identify the localized "regular" states.[4,5] For a 2D Hamiltonian, the NE of an eigenfunction is[4-8]

$$\Psi = \sum_l d_l f_l g_l,$$

where the natural orbitals $\{f_l\},\{g_l\}$ are uniquely defined and do not depend upon the choice of basis set. If the dominant configuration in the expansion is $\Phi_0 = f_{l_0}g_{l_0}$, then there is no other product function (within the same coordinate system) which has a better overlap with the exact eigenfunction. However, it is important to note that the natural expansion *is* variant under a unitary transformation of the coordinates. Therefore, there may be other sets of coordinates which provide a dominant term with a larger value than for the original set of coordinates. At a particular energy, the optimum coordinates are those for which the coupling terms in the Hamiltonian are minimized. By examining d_{max}^2 for different sets of coordinates, one can decide upon the optimum local coordinates.

Recently, it was pointed out[8] that the NE coefficient d_l^2 can be interpreted as the probability that a trajectory will be found near the phase space torus whose semiclassical quantization yields the separable wave function $f_l(q_1)g_l(q_2)$.

Prior to this study, the NE analysis had been applied to 2D systems by explicitly calculating all of the eigenvalues and eigenvectors of the Hamiltonian matrix. The apparent need to obtain all eigenvectors prevented extension of the NE method to highly excited states in 2D and larger systems. [For example, on the Cyber 170, we cannot solve the matrix eigenvalue problem for N (size of matrix) > 300.] The question naturally arose, "Can we perform the NE analysis *without* explicit knowledge of the wave function?" As we will demonstrate here, it is possible to generate the NE expansion without explicit knowledge of the eigenvectors. Our approach is based upon use of the recursive residue generation method[9,10] (RRGM), with a new feature—residue algebra—added.

If we consider the Green operator in the eigenvector basis,

$$G(E) = \sum_{\alpha} |\alpha\rangle\langle\alpha|/(E - E_\alpha),$$

the matrix elements in a zero-order basis $\{|n\rangle\}$ are given by

$$G_{nn'}(E) = \sum_{\alpha} \langle n|\alpha\rangle\langle\alpha|n'\rangle/(E - E_\alpha),$$

where $\langle n|\alpha\rangle\langle\alpha|n'\rangle$ is the *transition residue* at the pole E_α. The RRGM was developed in order to compute these residues *without* first finding any of the eigenvectors $\{|\alpha\rangle\}$. The RRGM has been applied to multiphoton absorption,[9-12] electronic absorption spectra,[13] thermally averaged correlation functions,[14] thermal reaction rate constants,[15] and percolation in lattices.[16] The method will then be reviewed in Sec. II and an extension, residue algebra, will be introduced. Applications to highly excited states in a model 2D system are presented in Sec. III.

II. NATURAL EXPANSION BY THE MODIFIED RRGM: THEORY

Prior to this study, natural expansions have only been applied to relatively low energy states of 2D model Hamiltonians.[4–8] For clarity, we shall repeat in Sec. III the NE analysis of an eigenstate for the two-mode system which was studied recently by Moiseyev et al.[5] The eigenstate $\Psi_\alpha(q_1,q_2) = |E_\alpha\rangle$ can be expanded in terms of a real-valued, separable, product basis

$$|n,m\rangle = \phi_n(q_1)\phi_m(q_2), \qquad (1)$$

such that

$$|E_\alpha\rangle = \sum_{n,m}^{\infty} |n,m\rangle\langle n,m|E_\alpha\rangle. \qquad (2)$$

Approximate eigenvector coefficients $C_{nm} = \langle n,m|E_\alpha\rangle$ can be computed by diagonalizing the Hamiltonian matrix $\mathbf{H} = \{\langle n',m'|H|n,m\rangle; n = 1,2,...,N_1; m = 1,2,...,N_2\}$.

The q_1 density kernel for state α,

$$\Gamma(q_1',q_1) = \int \Psi_\alpha^*(q_1',q_2)\Psi_\alpha(q_1,q_2)dq_2 \qquad (3)$$

is given by

$$\Gamma(q_1',q_1) = \sum_{n'n}^{N_1} A_{n',n}\phi_{n'}^*(q_1')\phi_n(q_1), \qquad (4)$$

where the symmetric density matrix $\mathbf{A}$ has elements,

$$A_{n'n} = \sum_m^{N_2} \langle n',m|E_\alpha\rangle\langle E_\alpha|n,m\rangle. \qquad (5)$$

The fact that the eigenvalues of $\mathbf{A}$ are the population probabilities of configurations in the NE of state $|E_\alpha\rangle$ can be seen as follows: Denote the eigenvalues and eigenvectors of $\mathbf{A}$ by $\{d_i\}$ and $\{D_i\}$, respectively. Then, the matrix elements $A_{n'n}$ can be constructed in the eigenvector representation

$$A_{n'n} = \sum_{l=1}^N D_{n'l}^* D_{nl}d_l^2. \qquad (6)$$

By substituting Eq. (6) into Eq. (4), we obtain the diagonalized density kernel

$$\Gamma(q_1',q_1) = \sum_{l=1}^{N_1} d_l^2 f_l^*(q_1')f_l(q_1). \qquad (7)$$

Similarly,[5] it is possible to diagonalize the density kernel $\Gamma(q_2',q_2)$. Such that

$$\Gamma(q_2',q_2) = \sum_l d_l^2 g_l^*(q_2')g_l(q_2) \qquad (8)$$

and by comparison with Eq. (3), one can get

$$\Psi_\alpha(q_1,q_2) = \sum_{l=1}^{\min(N_1,N_2)} d_l f_l(q_1)g_l(q_2). \qquad (9)$$

We have thus shown that $\{d_i^2\}$ are the eigenvalues of $\mathbf{A}$.

In conventional NE procedures, the matrix elements $\{A_{nm}\}$ are obtained by first computing the eigenvectors $\{\langle n,m|E_\alpha\rangle\}$ of the Hamiltonian matrix. The advantage of the RRGM[9,10] is that it enables A_{nm} to be evaluated without the need to calculate the eigenvectors of $\mathbf{H}$.

A. Matrix A by the RRGM

In the first step, the $N \times N$ Hamiltonian matrix is recursively converted into the $M \times M$ tridiagonal matrix $\mathbf{T}$:

$$\mathbf{U}^t\mathbf{H}\mathbf{U} = \mathbf{T}, \qquad (10)$$

where

$$\mathbf{U}_j^t\mathbf{U}_i = \delta_{ij},$$

$$\mathbf{T} = \begin{pmatrix} \alpha_1 & \beta_1 & 0 \cdots \\ \beta_1 & \alpha_2 & \beta_2 \\ 0 & \beta_2 & \alpha_3 \\ \cdot & & & \\ & \cdot & & \end{pmatrix}. \qquad (11)$$

The M comumn vectors $\mathbf{U}_j$, each of length N, are recursively developed by the Lanczos algorithm:

$$\beta_j\mathbf{U}_{j+1} = \mathbf{H}\mathbf{U}_j - \alpha_j\mathbf{U}_j - \beta_{j-1}\mathbf{U}_{j-1}, \quad (j = 1,2,...,M),$$
$$\alpha_j = \mathbf{U}_j^+\mathbf{H}\mathbf{U}_j,$$
$$\beta_j = \text{norm}[\mathbf{H}\mathbf{U}_j - \alpha_j\mathbf{U}_j - \beta_{j-1}\mathbf{U}_{j-1}], \quad \beta_0 = 0. \qquad (12)$$

To start the recursion, we prime the method with a starting vector $\mathbf{U}_1$. To simplify the notation, let the index k be defined from (n,m) and let l be attached to (n',m) such that

$$H_{kl} = \langle n,m|H|n',m\rangle. \qquad (13)$$

The normalized primer is then defined by $(i = 1,2,...,N)$

$$(\mathbf{U}_1)_i = \begin{cases} 0 & \text{if } i \neq k \text{ or } i \neq l, \\ 1/\sqrt{2} & \text{if } i = k \text{ or } i = l. \end{cases} \qquad (14)$$

From the tridiagonal matrix $\mathbf{T}$, the M eigenvalues $\{E_i\}$ are obtained. In addition, another set of $(M-1)$ eigenvalues $\{E_i^{(U)}\}$ can be obtained by diagonalizing the reduced matrix which is obtained from $\mathbf{T}$ by deleting the first row and column. It has been shown by Nauts and Wyatt[9,10] that the residues (squares of eigenvector coefficients)

$$R_U(E_\alpha,k,l) = \langle 1/\sqrt{2}(k+l)|E_\alpha\rangle^2 = \langle \mathbf{U}_1|E_\alpha\rangle^2 \qquad (15)$$

can be determined from these two sets of eigenvalues:

$$R_U(E_\alpha,k,l) = \frac{(E_\alpha - E_1^{(U)})}{(E_\alpha - E_1)} \cdots \frac{(E_\alpha - E_{\alpha-1}^{(U)})}{(E_\alpha - E_{\alpha-1})}$$
$$\times \frac{(E_\alpha - E_\alpha^{(U)})}{(E_\alpha - E_{\alpha+1})} \cdots \frac{(E_\alpha - E_{M-1}^{(U)})}{(E_\alpha - E_M)}, \qquad (16)$$

where E_α is the eigenvalue associated with the eigenfunction $|E_\alpha\rangle$ which we are attempting to analyze with the NE method. (Recall that M is the number of recursion steps.)

Similarly, we generate the residues R_v,

$$R_V(E_\alpha,k,l) = \langle 1/\sqrt{2}(k-l)|E_\alpha\rangle^2 = \langle \mathbf{V}_1|E_\alpha\rangle^2, \qquad (17)$$

by priming the Lanczos algorithm with the vector $\mathbf{V}_1$:

$$(\mathbf{V}_1)_i = \begin{cases} 0 & \text{if } i \neq k \text{ or } i \neq l, \\ 1/\sqrt{2} & \text{if } i = k, \\ -1\sqrt{2} & \text{if } i = l. \end{cases}$$

The residues $R_V(E_\alpha,k,l)$ are then computed from the two sets of eigenvalues $\{E_i\}$ and $\{E_i^{(V)}\}$. The desired transition residue in the $\mathbf{A}$ matrix [see Eq. (5)] is finally given by

$$\langle l|E_\alpha\rangle\langle E_\alpha|k\rangle = 1/2[R_U(E_\alpha,k,l) - R_V(E_\alpha,k,l)], \qquad (18)$$

and therefore, $A_{n'n}$ is obtained for each value of (k,l) from two sets of residues, which were computed without knowledge of any of the eigenfunctions.

B. The residue algebra

If N basis functions, $\{|n(i)m(i)\rangle; i = 1,2,...,N\}$ are used to evaluate $\mathbf{H}$, then approximately $N(N + 1)$ residues are needed when the RRGM is used to calculate the density matrix $\mathbf{A}$. Therefore, the CPU time required to build $\mathbf{A}$ will increase *nonlinearly* ($\sim N^2$) as N is increased. The residue algebra technique, which we will propose and test, will reduce the number of calculations so that the CPU time required to build $\mathbf{A}$ will increase only *linearly* as N is increased.

Let us assume that we wish to obtain *all* possible transition amplitudes among a given set of vectors, $\{|i\rangle, i = 1,2,...,N\}$ (in our case, $|i\rangle = |n,m\rangle$). Among this set of states, there are N diagonal "transitions" and $N(N - 1)/2$ off-diagonal transitions; there are thus a total of $N(N + 1)/2$ transitions to compute. Then, the *transition residues* (actually, residues of the transition amplitude) can be obtained formally if we know a set of intermediate amplitudes $\{\langle C|E_\alpha\rangle\}$:

$$\langle i|E_\alpha\rangle\langle E_\alpha|j\rangle$$
$$= [\langle i|E_\alpha\rangle\langle E_\alpha|C\rangle][\langle j|E_\alpha\rangle\langle E_\alpha|C\rangle]/[\langle C|E_\alpha\rangle]^2, \quad (19)$$

where $|C\rangle$ is the normalized *composite vector*,

$$|C\rangle = 1/\sqrt{N}[|1\rangle + |2\rangle + \cdots + |N\rangle]. \quad (20)$$

To compute all $N(N + 1)/2$ transition amplitudes, we will divide the calculation into two steps.

(1) The survival (diagonal) amplitude of the composite vector is computed, by initiating the Lanczos algorithm with the primer

$$(1/\sqrt{N}, 1/\sqrt{N},...,1/\sqrt{N}).$$

From this calculation, we obtain the N residues $\langle C|E_\alpha\rangle^2, \alpha = 1,2,...,N$.

(2) The transition amplitude between each "interesting" state $|i\rangle$ and the composite vector is computed. This in turn requires two recursion sequences, which are primed with the normalized vectors

$$|U_1\rangle = (|i\rangle + |C\rangle)/[2(1 + S)]^{1/2},$$
$$|V_1\rangle = (|i\rangle - |C\rangle)/[2(1 - S)]^{1/2}, \quad (21)$$

where S is the overlap between the nonorthogonal vectors $|i\rangle$ and $|C\rangle$,

$$S = \langle i|C\rangle = 1/\sqrt{N}. \quad (22)$$

From these two recursion sequences, we generate $2N$ residues, $\{\langle U_1|E_\alpha\rangle^2$, and $\langle V_1|E_\alpha\rangle^2; \alpha = 1,2,...,N\}$. The $i \rightarrow C$ transition residues are then generated from the equation

$$\langle i|E_\alpha\rangle\langle E_\alpha|C\rangle$$
$$= 1/2[(1 + S)\langle U_1|E_\alpha\rangle^2 - (1 - S)\langle V_1|E_\alpha\rangle^2]. \quad (23)$$

This can be verified by substituting Eq. (21) into the right-hand side of Eq. (23).

At this stage, we have $(N + 1)$ residues at each energy: $\langle i|E_\alpha\rangle\langle E_\alpha|C\rangle$, $i = 1,2...,N$ and $\langle C|E_\alpha\rangle^2$. From these we

are able to compute $N(N + 1)/2$ transition residues through Eq. (19). Thus, the residue algebra reduces the time required to compute $\mathbf{A}$ by a *factor* of $N/2$!

III. NATURAL EXPANSION BY THE MODIFIED RRGM: APPLICATION

A. Review of computational methods

Due to the propagation of roundoff error during the Lanczos recursion, some *spurious eigenvalues* (in the terminology of Cullum and Willoughby[17]) may be included when the eigenvalues of $\mathbf{T}$ are computed. The spurious eigenvalues are of two types:

(1) Uncovered eigenvalues which lie between accurate eigenvalues. Residues attached to these eigenvalues are always very small.

(2) "Ghost" eigenvalues which are multiple copies of eigenvalues which have converged. As the number of recursion steps increases, these ghosts gradually work in from both edges of the spectrum toward the interior. When an eigenvalue has attached ghosts, the net residue is split over the multiple copies. As a result, when a new ghost joins a set of (nearly) degenerate eigenvalues, the "old" total residue is split into more pieces, but the sum of all of the pieces is conserved.

As a result of the appearance of spurious eigenvalues, not all of the eigenvalues of $\mathbf{T}$ are eigenvalues of $\mathbf{H}$. This is why the number of recursions needed to generate all (or most) of the eigenvalues of $\mathbf{H}$ may exceed the size of $\mathbf{H}$.

In order to compute the residues from Eq. (16), it is preferable to remove the spurious eigenvalues from both lists, $\{E_\alpha\}$ and $\{E_\alpha^{(U)}\}$, before applying this formula. Cullum and Willoughby[17] have proposed and tested an efficient procedure for sorting out the spurious eigenvalues. If *only* the eigenvalues are desired, then it is important to remove the spurious ones.

In most physical problems, we are interested in *both* the eigenvalues and the residues (products of eigenvector coefficients). This is because the residues appear in expectation values of operators over the basis states. The presence of spurious eigenvalues is then of no consequence and Wyatt and Scott[18] have developed another method for computing *all* of the eigenvalues and residues from the tridiagonal matrix. Unlike the Cullum–Willoughby procedure, this method does not require removal of spurious eigenvalues by comparing lists of eigenvalues. This method computes the eigenvalues of $\mathbf{T}$ and the squares of the coefficients in the first row (only) of the eigenvector matrix of $\mathbf{T}$. These squares are the residues ($\langle U_1|E_\alpha\rangle^2$ or $\langle V_1|E_\alpha\rangle^2$) that we seek. The method "works" because unconverged "incorrect" eigenvalues have very small residues and multiple copies merely share the overall "strength" (total residue) associated with a given pole of the Green operator.

B. Numerical example

In this section, calculation of the natural expansion coefficients by the RRGM with and without residue algebra will be illustrated. As an example, we will study the 2D Pul-

len–Edmonds[19] (PE) Hamiltonian

$$H = \frac{1}{2}\left(\frac{-\partial^2}{\partial q_1^2} + q_1^2\right)$$
$$+ \frac{1}{2}\left(\frac{-\partial^2}{\partial q_2^2} + q_2^2\right) + \lambda q_1^2 q_2^2. \qquad (24)$$

This is the simplest model which exhibits both classical and quantal transitions[19,20] from regular to chaotic behavior. The parameter λ (usually, $\lambda = 0.05$) plays the role of $\hbar$, as can be seen by making the transformations $q_i \to q_i/\lambda^{1/2}$. It has been found that if E is high enough ($E \rangle 15$), the trajectories are mostly chaotic[19] and the eigenfunctions are chaotic in the sense that they tend (when smoothed) to fill uniformly the available phase space.[21] In such a case, these chaotic eigenfunctions are far from separability (since they cannot be assigned good quantum numbers) and the static SCF method is not applicable.[22] However, it was found recently that these "chaotic eigenfunctions" can be described by just a few natural configurations.[8] (This is in spite of the conjecture that many random components are needed to describe chaotic eigenfunctions.)

Our strategy is as follows:

(1) Construct the density matrix A by the RRGM (without using eigenvectors of H and without use of the residue algebra) and compare the eigenvalues of A (which are the population of the natural configurations) with previous results which were obtained by the conventional NE method[8] (i.e., *with* eigenvectors of H).

(2) Repeat the RRGM calculations, but employ the residue algebra, as described in Sec. II B. As a result of this comparison, we will show that use of the new algebraic technique significantly speeds up the calculations and enables us to study large systems which could not be studied before, at least on the Cyber 170.

In order to find the A_1 symmetry eigenfunctions of the PE Hamiltonian, N even parity basis functions were constructed from a direct product of harmonic oscillator functions,

$$|i(l_1,l_2)\rangle = \begin{cases} 1/\sqrt{2}[\phi_n(q_1)\phi_m(q_2) + \phi_m(q_1)\phi_n(q_2)], \\ n \neq m, \\ \phi_n(q_1)\phi_n(q_2), \\ n = m, \end{cases}$$
$$(25)$$

where $i = 1,2,...,N, l_1 = \max(n,m)$, $l_2 = \min(n,m)$. The Hamiltonian matrix elements are given in Ref. 19.

In order to obtain the density matrix A, Eq. (18) should be modified slightly to accomodate the symmetry restriction in Eq. (25). In our case, the elements of A are given by

$$A_{ij} = \sum_m \langle i(l_1',l_2')|E_\alpha\rangle\langle E_\alpha|j(l_1,l_2)\rangle f(i)f(j), \qquad (26)$$

where

$$l_1' = \max(n',m), \quad l_1 = \max(n,m),$$
$$l_2' = \min(n'm), \quad l_2 = \min(n,m). \qquad (27)$$

in which i and j are associated with (n',m) and (n,m) as

shown in Eq. (27). In addition, the symmetry factors are given by

$$f = \begin{cases} 1 & \text{if } n = m \text{ (or } n' = m), \\ 1/\sqrt{2} & \text{if } n \neq m \text{ (or } n' \neq m). \end{cases} \qquad (28)$$

To avoid computation of the eigenvectors, $|E\rangle$, of the matrix H, we used the RRGM as described above:

$$\langle i|E_\alpha\rangle\langle E_\alpha|j\rangle = 1/2[\langle U|E_\alpha\rangle^2 - \langle V|E_\alpha\rangle^2], \qquad (29)$$

where $|U\rangle = (|i\rangle + |j\rangle)/\sqrt{2}$ and $|V\rangle = (|i\rangle - |j\rangle)/\sqrt{2}$ are the two starting vectors used by the RRGM to bring H into tridiagonal form (T). The residues, $\langle U|E_\alpha\rangle^2$ or $\langle V|E_\alpha\rangle^2$ are obtained from the first row of the eigenvector matrix of T (see Sec. III A on the Wyatt and Scott[18] method).

The number of recursions used here (M) were about $2N$ (N is the dimension of H)—this ensures accurate eigenvalues for T (and H). The accuracy criterion was that all eigenvalues of T which were obtained from the two starting vectors (U_1 or V_1) used to prime the Lanczos algorithm should agree within a specified tolerance, $\Delta E \leqslant 0.005$.

The eigenvalues of A computed via the RRGM were compared with the population probabilities obtained by the conventional procedure[8] (i.e., calculate $|E_\alpha\rangle$). The RRGM values were accurate to within 1×10^{-6} of the exact values! The NE results for seven low eigenvalues and three high eigenvalues are listed in Table I. However, as N increases, the CPU time becomes prohibitively large, as shown in Fig. 1. In fact, on the Cyber 170, it was not possible to go above $N = 200$.

TABLE I. Natural expansions using the RRGM: $N = 300$, $M = 500$.[a]

E_α	$d_i^{2\,b}$	E_α	d_i^2
1.012 069	0.999 663	28.943 228	0.427 778
			0.293 929
3.079 643	0.529 800		0.109 954
	0.470 156		0.109 134
			0.025 470
5.075 339	0.453 161		0.003 930
	0.438 418		0.003 883
	0.108 401		0.000 434
			0.000 428
5.302 0623	0.892 321	29.098 270	0.239 597
	0.058 389		0.152 751
	0.049 306		0.087 705
			0.085 749
7.126 805	0.489 350		0.068 529
	0.485 298		0.064 530
	0.014 218		0.047 497
	0.011 164		0.045 159
			0.005 054
7.607 216	0.548 890		0.004 983
	0.426 823		0.000 193
	0.012 854		0.000 193
	0.011 453		
9.154 836	0.475 244	29.444 299	0.480 814
	0.473 799		0.480 811
	0.023 544		0.016 491
	0.022 048		0.016 488
			0.002 378
			0.002 376
			0.000 312
			0.000 310

[a] All eigenvalues in the range $0 < E_\alpha < 30$ were analyzed, but only some of them are shown here.
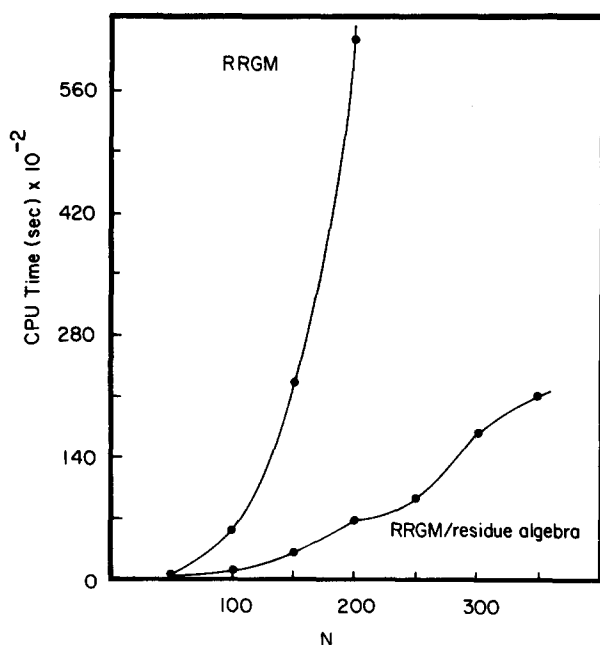[b] Only values of d_i^2 larger than 0.0001 are listed here.

FIG. 1. CPU time requirement (on the Cyber 170/750) for RRGM calculations with and without the residue algebra. N is the basis size.

Use of the residue algebra significantly reduced the CPU requirement of the RRGM calculations. To emphasize the role of residue algebra, Eq. (26) is rewritten

$$A_{ij} = \sum_m f(i) f(j) \left[\langle i(l'_1, l'_2) | E_\alpha \rangle \langle E_\alpha | C \rangle \right]$$
$$\cdot \left[\langle j(l_1, l_2) | E_\alpha \rangle \langle E_\alpha | C \rangle \right] / \left[\langle C | E_\alpha \rangle^2 \right], \quad (30)$$

where the indices are defined in Eqs. (25) and (27) and all of the residues $[\langle \cdots | E_\alpha \rangle \langle E_\alpha | \cdots \rangle]$ were obtained by the RRGM [see Eq. (29)]. As expected, the time required to compute the residues was reduced by a factor of $N/2$. The coefficients in the NE analysis obtained with the algebraic technique are in complete agreement with the previous results.[8]

The deviation from linearity in the dependence of CPU time upon N, obtained in the RRGM-residue algebra calculations, arises from two sources.

(a) Different numbers of recursion steps (M) were required for the different basis sizes.

(b) The routine used to compute eigenvalues of the tridiagonal matrix (the QL algorithm) has its own dependence upon N, beyond the linear dependence in the residue algebra calculations.

Several comments should be made with regard to the computation times reported here, which are large even for the residue algebra method (20 900 CPU s, for a 350×350 matrix). First, the matrix multiplication algorithm is completely unoptimized; optimization can reduce times by substantial amounts. Vectorization on a supercomputer (Cray or Cyber 205) can further reduce times by factors[23] of 50–100. These improvements alone make calculation on matrices of several thousand basis functions amenable.

A second crucial point concerns the number of recur-

sion steps required per Green's function matrix element. It should be possible to decrease this by a factor of 5–10 by employing canonical transformations on the Hamiltonian and/or the initial Lanczos vectors, even for strongly coupled systems like the one studied here by us,[11,16] recursion numbers on the order of 5%–10% of the matrix dimension have produced effective convergence.

Finally, the present application (to the NE) requires computation of *all* Green's function matrix elements. For many other uses (e.g., statistical mechanics involving two-particle Green's functions) only a small fraction of elements are required. In such cases, the advantage of the residue algebra version of the RRGM over conventional diagonalization procedures becomes overwhelming.

In using the RRGM (even with residue algebra), the price that we have to pay is measured in CPU time. Yet, the method allows us to study larger systems than could be previously studied. For example, on the Cyber 170, we could not carry out standard RRGM calculations of NE coefficients for $N > 200$ nor could we carry out the direct analysis by calculating the eigenvectors of the Hamiltonian matrix for $N > 250$. As can be seen in Fig. 1, the use of residue algebra significantly reduces the CPU requirements and thus permits NE analysis on larger systems.

IV. SUMMARY

The natural expansion method offers a systematic way to identify localized states which can be assigned "good" quantum numbers, even in the "quasicontinuum." The identification of such localized highly excited states is important in investigating the possibility of mode specific reactions. In the natural expansion, coefficients of the "optimal" product function (optimal in the sense that there are no other product functions which have a higher overlap with the exact wave function) are calculated. The square of the natural expansion coefficent of the dominant configuration, d^2_{max}, measures the strength of the coupling between the two modes ($d^2_{max} \to 1$ as coupling $\to 0$) and the applicability of the local mode approximation.

Prior to this study, natural expansions have been limited to relatively small model Hamiltonians, since *all* eigenvectors of H were computed and stored. However, through use of the RRGM, the natural expansion analysis can be performed without the need to compute eigenvectors of H. Use of the RRGM then enables us to study larger systems which could not be studied before, due to limitations on computer storage. However, the price we pay in using the RRGM is measured in CPU time.

The residue algebra, a method to obtain all transition amplitudes among a set of states, is presented and used here. This method reduces the number of calculations so that the CPU time required to build the density matrix increases only linearly as the size of the basis increases. To illustrate the applicability of the modified RRGM, we studied a two-mode system, most of whose excited states cannot be assigned good quantum numbers.

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