THE LANCZOS ALGORITHM IN MOLECULAR DYNAMICS: CALCULATION OF SPECTRAL DENSITIES

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In the past the Lanczos algorithm has proven to be a very useful tool
in the study of molecular dynamics. It enables efficient calculation
of the spectral densities which are essential in the interpretation of
spectroscopic or scattering experiments. In the present work, the use
of the Lanczos algorithm in the calculation of the spectral densities
is analyzed in a general fashion. Its application to problems
characterized by complex symmetric matrices, which are normally
encountered in the analysis of magnetic resonance experiments, is then
recovered as a particular case. After a discussion of the factors
influencing the convergence in the calculation of spectral densities,
the implementation of the Lanczos algorithm with non-orthogonal basis
functions is considered in relation to molecular systems having
hindered degrees of freedom.

INTRODUCTION

The direct observation of molecular motion in condensed phases is possible
only in so-called Molecular Dynamics (M.D.) "experiments", i.e. in computer
simulations of trajectories of systems of particles (of the order of hundreds or
thousands) to model macroscopic samples. Information about the molecular motion
in real systems, mostly obtained by means of spectroscopic or scattering techni-
ques, is instead very indirect. One is confined to the measurement of the
macroscopic response to some external, time-dependent, perturbing field.
According to linear response theory [1], the spectroscopic observation is
characterized by a particular spectral density, which is the Fourier-Laplace
transform of the time correlation function(s), for the dynamical variable(s)
probed in the specific experiment. Formally, the spectral densities are the
matrix elements of the resolvent constructed from the time evolution operator,
Γ, appropriate for the system observed. By considering a proper basis set, the
resolvent can be written in terms of the matrix representation of Γ, and it can
be solved by numerical methods.

By means of spectroscopic techniques like:

- magnetic resonance (ESR and NMR)
- dielectric relaxation
- light scattering
- infrared and Raman spectroscopy
- incoherent neutron scattering

one can have access to spcific spectral densities and infer, from a postulate of
Γ, information about the translational, rotational, and conformational motion of
the molecules constituting the observed system.

The calculation of the spectral densities can be seen as a fundamental tool in

the interpretation of spectral data, since it is a necessary step in relating experimental measurements and theoretical models for Γ. This explains the need for specific algorithms which should be efficient from the points of view of both the speed of calculation and the size of the matrix that can be handled. The development of sophisticated models of motion where the coupling among several degrees of freedom is taken into account, constitutes a natural trend in chemical physics that is required by improvements in experimental techniques which lead to more detailed knowledge of the spectral densities. Correspondingly, one must tackle calculations of spectral densities from larger matrix representations, and the efficiency of the algorithm becomes critical in making possible the interpretation of spectral information.

The Lanczos algorithm [2-4] constitutes a natural choice as a method of calculation of the spectral densities, since the matrices normally encountered are very sparse [5,6]. Indeed, the Lanczos algorithm is particularly suitable because it produces a tridiagonal matrix, such that the continued fraction representation of the spectral density is easily generated from the elements of this tridiagonal matrix. This allows for a direct calculation of the frequency dependence of the spectral density without the need for the eigenvalues. Moreover the results of the Lanczos algorithm can be related [7] to the continued fraction representation of the spectral densitites derived by H. Mori [8], thereby connecting a numerical method to the projective formalisms often used in statistical mechanics [9].

In the next section, the formal definitions of the quantities related to spectral densities and spectra will be given, with particular emphasis on classical systems. After a brief discussion of the most common models of motion, the results of linear response theory will be summarized. This will constitute the framework for the subsequent analysis of the role played by the calculation of spectral densities in the theoretical interpretation of spectroscopic data.

The numerical calculation of spectral densities by means of the Lanczos algorithm will be the central topic of the third section. First, the method will be illustrated with self-adjoint, "symmetrized," time evolution operators. Then the general case will be considered, showing how the coefficients of the continued fraction representation are calculated by numerical implementation of the Lanczos algorithm. The performance of the algorithm will be discussed specifically in connection with the convergence of the continued fraction solution. Particular emphasis will be given to the following result: the Lanczos algorithm is more efficient in producing the overall shape of the spectral lineshape than in computing the eigenvalues of the related matrix.

The final part of the third section will be devoted to a discussion of the criteria for the choice of the basis functions necessary to generate the matrix representation of the time evolution operator. Such a choice is an important ingredient in actual calculations, and it must be carefully considered, case by case, in order to minimize computational effort. Particular emphasis will be given to problems characterized by strong confining potentials, for which a large reduction of the size of the matrices can be achieved by means of non-orthogonal basis functions. Therefore the implementation of the Lanczos algorithm with non-orthogonal functions will also be presented.

In the summary section, we shall point out some further applications of the Lanczos algorithm to the study of the molecular dynamics, and we suggest where further computational developments would be desirable.

SPECTRAL DENSITIES AND MOLECULAR MOTION

In this section, the correlation function formalism and the results of linear

response theory will be summarized in order to present a clear definition of the quantities to be computed by means of the Lanczos algorithm.

We consider a system described by an ensemble of M classical stochastic variables $z = (z_1, z_2, ..., z_M)$; (the generalization to quantum system will be presented subsequently). The stationary state of the system is described by the equilibrium distribution function $P_{eq}(z)$, defined as the probability density with respect to the infinitesimal volume $d^M z = dz_1 dz_2 .... dz_M$. The equilibrium average of a dynamical variable described by the function $A(z)$ is then calculation according to the following integral:

$$\bar{A} = \int d^M z \, P_{eq}(z) A(z) \tag{2.1}$$

One can now introduce the Hilbert space ε constituted from the ensemble of dynamical variables having well defined average values, and for which the following formal definition of scalar product applies:

$$\langle A_1 | A_2 \rangle = \int d^M z \, A_1(z)^* A_2(z) \tag{2.2}$$

The dynamics of the system is characterized by the time evolution operator Γ which determines the behavior of the non-equilibrium distribution function $P(z; t)$:

$$\partial/\partial t \, P(z ; t) = -\Gamma P(z ; t) \tag{2.3}$$

Hereafter we shall consider only stationary Markovian processes [10]; that is we assume that Γ does not depend explicitly on the time, and we take P_{eq} to be the unique stationary solution Γ:

$$\Gamma P_{eq} = 0 \tag{2.4}$$

For a given pair of dynamical variables $A_1(z)$ and $A_2(z)$, the time correlation function $G(t)$ is defined in terms of the following dynamical average [11]:

$$G(t) = \overline{A_1[z (t)] \, A_2[z (o)]} \tag{2.5}$$

which, from the formal solution of eq. (2.3), can be written explicitly as follows:

$$G(t) = \langle A_1 | \exp(-\Gamma t) | P_{eq} A_2 \rangle \tag{2.6}$$

The corresponding spectral density $J(\omega)$, which is the Fourier-Laplace transform of $G(t)$, is written as:

$$J(\omega) \equiv \int_0^\infty dt \, \exp(-i\omega t) \, G(t) = \langle A_1 | (i_\omega + \Gamma)^{-1} | P_{eq} A_2 \rangle \tag{2.7}$$

The internal motion of a mobile group in a molecule can be taken as a model system for illustrating the previous statistical concepts. The stochastic variable is now represented by the angle θ, which is the angle of rotation of the mobile group around a fixed axis of the rigid part of the molecule. The equilibrium distribution function is normally written as:

$$P_{eq}(\theta) = \exp\{-V(\theta)/kT\}/\int_0^{2\pi} d\theta \, \exp\{-V(\theta)/kT\} \tag{2.8}$$

where $V(\theta)$ is the mean potential acting on the mobile group.

It results from the interaction of the mobile group with the rigid part of the molecule. There the minima of $V(\theta)$ determine the stable conformations of the system. See for example reference 12 for a parametric form of $V(\theta)$ often used

in the study of conformational dynamics of alkyl chains. The dynamics of the internal rotor can be represented by different operators Γ, the choice depending on the type of coupling with the thermal bath. A quite common model, justified on physical grounds when dealing with bulky mobile groups, is provided by the diffusion operator, which, for the internal motion problem being used for illustration, is written as follows:

$$\Gamma = -D(\partial/\partial\theta)\, P_{eq}(\partial/\partial\theta)\, P_{eq}^{-1} \qquad (2.9)$$

where D is the diffusion coefficient. Similar diffusion operators can be generated when dealing with the molecular translational and rotational motion and their coupling [13,14]. A more general class of time evolution operators are represented by the so-called Fokker-Planck equations, where the classical streaming motion is taken into account by considering as stochastic variables both the coordinates and the conjugate momenta [9,13,15,16]. Therefore, statistical mechanics provides a hierarchy of models of motion, where the complexity (i.e. the number of degrees of freedom explicitly taken into account) grows with the level of generality and with the accuracy in representing the dynamical features of the physical system (e.g. ref. 17).

Let us now briefly illustrate, in the context of classical systems, the linear response theory which constitutes the general framework for the interpretation of spectroscopic measurements [11]. Such experiments are characterized by the presence of an external oscillating field, having strength $|E_0|$ and frequency ω, which is coupled to a given dynamical variable $B(z)$ of the system, yielding a contribution to the total energy as $B(z)|E_0|\cos\omega t$. The response of the system to the external field is observed by measuring the macroscopic average of a specified dynamical variable $A(z)$. Dielectric relaxation experiments, for example, are characterized by an oscillating electric field $E(t) = E_0 \cos\omega t$, that interacts with the molecular dipoles $\mu(t)$, which have a time-dependent orientation as a consequence of the rotational motion of the molecules. Therefore $B(z)$ is given by $|\mu|\cos\beta$, where the stochastic variable β is defined as the angle between μ and E_0. The observed macroscopic variable is represented by the polarization of the medium, in practice the average of the components of the dipole moments along E_0, i.e. $A(z) = B(z)$.

By assuming that the external field acts as a small perturbation with respect to the dynamical behavior of the isolated system, it is shown that the macroscopic average of $A(z)$ oscillates around its equilibrium value $\bar{A}$ with the same frequency ω of the field, and that the intensity of these oscillations is proportional to the field strength $|E_0|$ according to the frequency dependent susceptibility $\chi(\omega)$ [1]. On the other hand, the susceptibility $\chi(\omega)$ is independent of the external perturbation, and it is determined by the dynamics of the isolated system described by the time evolution operator Γ, according to the following equation [1]:

$$\chi(\omega) = -i\omega J(\omega) + \overline{\delta A^* \delta B} \qquad (2.10)$$

where $J(\omega)$ is the spectral density that relates to the pair of dynamical variables $\delta A = A(z) - \bar{A}$ and $\delta B = B(z) - \bar{B}$. That is:

$$J(\omega) = \langle \delta A | (i\omega + \Gamma)^{-1} | P_{eq}\, \delta B \rangle \qquad (2.11)$$

It is implicit that each spectroscopy corresponds to a specific choice for the pair of dynamical variables A and B. It should be noted that the susceptibility is a complex quantity, its real and imaginary parts being respectively related to the in-phase and to the out-of-phase response of the system to the oscillatory perturbation. Often one measures only one component, more precisely the imaginary part, which in the following, will be identified with the observed spectral lineshape $I(\omega)$:

$$I(\omega) \equiv -\chi''(\omega) = \omega Re\{J(\omega)\} \qquad (2.12)$$

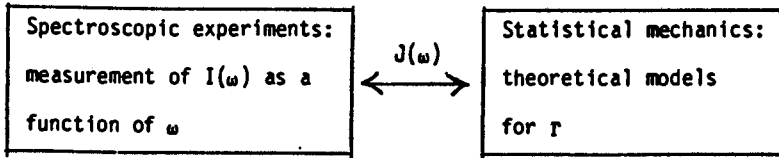| Spectroscopic experiments: measurement of $I(\omega)$ as a function of ω	$J(\omega)$ $\longleftrightarrow$	Statistical mechanics: theoretical models for Γ

Figure 1

As sketched in Figure 1, the calculation of the spectral density is an essential step in relating the experimental results to the theoretical model for the dynamical behavior of the system. Only by a careful comparison of the frequency dependence of the theoretical $J(\omega)$ with the experimental data, is it possible to obtain a full account of the effects of the molecular motion on the observed spectra. Ideally, one would like to perform the "inverse transform", viz. to reconstruct the detailed form of Γ from a given experimental $I(\omega)$. Unfortunately, $I(\omega)$ supplies very limited and incomplete information. Instead one would need all the correlation functions for a complete set of dynamical variables which span the vector space implicit in eq. (2.2).

More realistically one compares the theoretical and the experimental $I(\omega)$ in order to achieve the following two objectives:

i) the verification of the adequacy of the theoretical model Γ. In this context one often compares the experimental results with the theoretical profiles of $I(\omega)$ obtained with different models of motion in order to assess which one is the most appropriate.

ii) The determination of the values of the transport coefficients, [such as the diffusion coefficient D in eq. (2.9)], which enter as parameters in the expression of Γ. A best fit between theoretical and experimental $I(\omega)$ supplies the optimal estimate of these parameters.

In the most favorable situations, i.e. when the experimental spectrum $I(\omega)$ is known accurately over a wide range of frequencies, the calculation of the spectral density provides detailed information on both the type of molecular dynamics and the characteristic relaxation time associated with each elementary motion.

The need for calculating spectral densities is clear in the context of standard spectroscopies such as magnetic resonance or dielectric relaxation measurements. The same conclusion also follows from the analysis of scattering experiments. As an example, the differential cross section for incoherent neutron scattering is proportional to the real part of the following spectral density [18]:

$$J(\omega) = \langle \exp(-i\mathbf{q} \cdot \mathbf{r})|(i\omega + \Gamma)^{-1}|P_{eq}\exp(-i\mathbf{q} \cdot \mathbf{r})\rangle \qquad (2.13)$$

where Γ is now the time evolution operator appropriate for the stochastic variable $\mathbf{r}$, the vector position of the scattering nucleus. The vector $\mathbf{q}$ and $\hbar\omega$ are respectively the momentum and energy differences between incident and scattered neutrons.

Up to now we have considered classical stochastic variables. In the analysis of experiments like magnetic resonane (NMR or ESR) it is necessary to deal with quantum degrees of freedom, i.e. electronic and nuclear spin, and their interaction with the molecular orientational degrees of freedom specified by the

Euler angles $\Omega = (\alpha,\beta,\delta)$. The latter are usually taken as classical stochastic variables for motions in condensed phases. In these cases the dynamics of the system is usually described by the so-called stochastic Liouville operator [19,20], written as:

$$\Gamma = \Gamma_\Omega - (i/\hbar)H(\Omega)^X \qquad (2.14)$$

where Γ_Ω is the stochastic time evolution operator for just the orientational variables (e.g. the diffusion operator), and $H^X \equiv [H, \ ]$ is the quantum-mechanical time propagator (superoperator). Note that the coupling between the quantum and classical degrees of freedom, for example the modulation of the energy of the quantum states induced by the rotational motion, is implicitly taken into account by the dependence of H upon the orientational variable Ω. The correlation function in eq. (2.6) and the corresponding spectral density of eq. (2.7), where A is now an operator on the quantum states, are calculated with the previous stochastic Liouville operator Γ, after redefining the scalar products as:

$$\langle\cdots\rangle \equiv \text{Tr} \int d\Omega \cdots \qquad (2.15)$$

i.e. as a trace over the quantum states and integration over the classical stochastic variables.

For the sake of simplicity, in the next section we shall focus on classical systems, such that the time evolution operator can easily be represented in a basis of functions of the stochastic variables. However the numerical methods we discuss can also be applied to problems described by the stochastic Liouville operator of eq. (2.14) if a proper basis for the quantum degrees of freedom is specifically considered [21].

CALCULATION OF SPECTRAL DENSITIES BY MEANS OF THE LANCZOS ALGORITHM

In the analysis of the computational methods, it is convenient to make reference to the so-called "symmetrized" time evolution operator $\tilde{\Gamma}$ defined as follows [22].

$$\tilde{\Gamma} = P_{eq}^{-1/2} \ \Gamma P_{eq}^{1/2} \qquad (3.1)$$

The spectral density of eq. (2.11) becomes:

$$J(\omega) = \langle P_{eq}^{1/2} \ \delta A | (i_\omega + \tilde{\Gamma})^{-1} | P_{eq}^{1/2} \ \delta B\rangle \qquad (3.2)$$

The reasons which dictate such a transformation of Γ are twofold. First of all, when dealing with autocorrelation functions, i.e. A=B, the corresponding spectral density is simply the diagonal matrix element of the resolvent operator with respect to the function $P_{eq}^{1/2} \ \delta A$ (i.e. right- and lefthand vectors are Hermitian conjugates). Most observables are related to the autocorrelation functions as we previously pointed out, [e.g. eq. (2.13) or the discussion of dielectric relaxation in the previous chapter]. Secondly this transformation on Γ clarifies the symmetries of the time evolution operator. As an example, if Γ is given by a diffusion operator such as eq. (2.9), its symmetrized form is self-adjoint with respect to the definition eq. (2.2) of the scalar product. This property is not, in general, shared by the symmetrized Fokker-Planck operators or the stochastic Liouville operators. But for them it is possible to generate complex symmetric matrix representations by a careful choice of the basis functions [6,21], and this will simplify the computational algorithm that is needed.

We first consider the calculation of the spectral density under the simplifying conditions that Γ is self-adjoint and that A=B. If A≠B, then it is easy to show that $J(\omega)$ of eq. (3.2) can be decomposed as a linear combination of spectral

densities associated with the autocorrelation functions for the dynamical variables A-B and A+B [6].

Once a suitable basis set of functions for the stochastic variables z has been introduced, one can apply the Lanczos algorithm [2-4] to the matrix representation of $\bar{\Gamma}$. Alternatively, the methodology, which is more general than just the numerical algorithm, can be applied directly to the operator $\bar{\Gamma}$, in order to produce an orthonormal set of functions ϕ_j (z). We shall follow the second route because of its connection with the method of moments [23] and with the projective schemes frequently used in statistical mechanics [9].

Given the relation eq. (3.2) for the spectral density, a natural choice for the first element of the basis set is represented by the function $P_{eq}^{1/2} \delta A$ properly normalized:

$$\phi_1(z) = P_{eq}^{1/2} \delta A / \langle \delta A | P_{eq} | \delta A \rangle^{1/2} \tag{3.3}$$

The remaining functions ϕ_j(z) are generated iteratively according to the following relation:

$$\beta_{n+1}\phi_{n+1} = (1-P_n)\bar{\Gamma}\phi_n \tag{3.4}$$

where β_{n+1} is the real coefficient implicitly defined by the normalization condition (i.e. $\langle \phi_{n+1} | \phi_{n+1} \rangle = 1$), and P_n is the projection operator on the subspace spanned by functions $\phi_1, \phi_2, \ldots, \phi_n$:

$$P_n = \sum_{j=1}^{n} |\phi_j\rangle\langle\phi_j| \tag{3.5}$$

It is easily demonstrated that $\bar{\Gamma}$ has a tridiagonal representation in the ϕ-basis (i.e. $\langle \phi_j | \bar{\Gamma} | \phi_{j'} \rangle = 0$ for $|j-j'|>1$) and that:

$$\beta_j = \langle \phi_j | \bar{\Gamma} | \phi_{j-1} \rangle \tag{3.6}$$

Therefore, a three term recursive relation is obtained from eq. (3.4), written as:

$$\beta_{n+1}\phi_{n+1} = (\bar{\Gamma} - \alpha_n)\phi_n - \beta_n \phi_{n-1} \tag{3.7}$$

where the α_j's are the diagonal elements of Γ in the ϕ-basis:

$$\alpha_j = \langle \phi_j | \bar{\Gamma} | \phi_j \rangle \tag{3.8}$$

In the ϕ-representation, the spectral density is written as:

$$J(\omega) = \overline{|\delta A|^2} \, [(i_\omega 1 + T)]_{1,1} \tag{3.9}$$

coefficients α_j and β_j previously defined.

An elementary application of the theorem of matrix partitioning, allows one to write down the frequency dependence of $J(\omega)$ according to the following continued fraction [24]:

$$J(\omega)/\overline{|\delta A|}^{2} = \cfrac{1}{i_\omega + \alpha_1 - \cfrac{\beta_2^2}{i_\omega + \alpha_2 - \cfrac{\beta_3^2}{i_\omega + \alpha_3 \cdot}}} \tag{3.10}$$

Therefore the application of the Lanczos algorithm to the abstract Hilbert space in which $\hat{\Gamma}$ is defined, generates the continued fraction representation of the spectral density. The same result, apart from the identification of $\hat{\Gamma}$ with the classical Liouville operator, has been derived by H. Mori in the context of the dynamics of systems of interacting particles [8]. As matter of fact, the same methodology, more specifically the recursive equation (3.4), is the foundation of both the Lanczos algorithm and Mori's derivation [7]. It is interesting to note that this connection between numerical methods and the formalisms of theoretical physics, can be extended further, by considering on the one hand the block Lanczos algorithm [25], and on the other hand the projective scheme normally used for deriving a diffusion or Fokker-Planck equation from the classical dynamics of an ensemble of interacting particles [9,13].

The relation specified by the continued fraction in eq. (3.10) is quite general. Analytical calculation of the coefficients α_j and β_j from the explicit operator form of $\hat{\Gamma}$ is in principle possible. Practically, however, this can be pursued only for the first few coefficients. Therefore numerical implementation of the recursive relation eq. (3.7) is essential in calculating enough coefficients of the continued fraction for an accurate simulation of the frequency dependence of $J(\omega)$. In practice, one generates the matrix representation M of the symmetrized operator $\hat{\Gamma}$ in a given basis set of orthonormal functions $f_j(z)$:

$$M_{jk} = \langle f_j | \hat{\Gamma} | f_k \rangle \qquad (3.11)$$

From eq. (3.7), the standard recursive relation of the Lanczos algorithm is readily obtained in the following form:

$$\beta_{n+1} \, x_{n+1} = (M - \alpha_n 1) \, x_n - \beta_n \, x_{n-1} \qquad (3.12)$$

with the column matrix x_n containing the expansion coefficients of ϕ_n:

$$\phi_n = \sum_j (x_n)_j \, f_j \qquad (3.13)$$

The standard computer implementation of the Lanczos algorithm [3,4] can then be used for calculating the coefficients α_j and β_j, and from those the frequency profile of $J(\omega)$ according to the continued fraction representation of eq. (3.10).

In order to complete this discussion we must deal with the calculation of the starting vector x_1. Given eq. (3.3) for ϕ_1, one can obtain the $(x_1)_j$ of eq. (3.13) by computing the scalar products $\langle f_j | \phi_1 \rangle$. This direct approach has been used frequently. However, it usually requires numerical integrations which can become unwieldy for several degrees of freedom. An alternative approach is to consider the following expression [See eqs. (2.4) and (3.1)] [26]:

$$\lim_{s \to 0^+} [s1 - M] \, x_0 = c \qquad (3.14)$$

where x_0 is the vector representation of $P_{eq}^{1/2}$ and c is an arbitrary ("initial") vector. this follows because $P_{eq}^{1/2}$ is the unique stationary solution of $\hat{\Gamma}$. One solves eq. (3.14) by matrix inversion techniques to obtain x_0 for the limit of very small s. Then

$$(x_1)_j = \sum_k \langle f_j | \delta A | f_k \rangle (x_0)_k \qquad (3.15)$$

Eq. (3.15) is easy to evaluate, since we usually choose basis functions f_j that bear a simple relation to the δA (and δB) of interest.

The calculation of spectral densities from the recursive relation eq. (3.12) can easily be generalized to operators $\tilde{\Gamma}$ which are not self-adjoint, but which have a complex symmetrix matrix representation M. In previous work [6], we have shown that eq. (3.12) continues to hold, but with the column matrices x_n now normalized without complex conjugation (i.e. the complex conjugation must be removed from the definition of scalar product between arrays). However, we now wish to rederive this result in a more general context, by considering the calculation of spectral densities for a general $\tilde{\Gamma}$. Moreover we also relax the previously assumed condition A=B. This general case is related to the implementation of the Lanczos algorithm to non-symmetric matrices, which leads to a biorthonormal basis set [27, 28]. When we conside the functions ϕ_j that we have introduced above, we would now have to recognize that for the non-self-adjoint operator, their iterative generation will now lead to a biorthonormal set of functions ϕ_j and ϕ^j :

$$\langle \phi_j | \phi^{j'} \rangle = \delta_{j,j'} \qquad (3.16)$$

starting from the ϕ_1 and ϕ^1 calculated from the right-hand and left-hand vectors of the spectral density of eq. (3.2), according to the following relations:

$$\phi_1 = P_{eq}^{1/2} \, \delta A / \langle \delta B | P_{eq} | \delta A \rangle^{1/2} \qquad (3.17a)$$

$$\phi_1 = P_{eq}^{1/2} \, \delta B / \langle \delta A | P_{eq} | \delta B \rangle^{1/2} \qquad (3.17b)$$

Instead of eq. (3.4) we now have a generating equation for each type of basis function:

$$\beta_{n+1} \, \phi_{n+1} = (1 - P_n)\tilde{\Gamma}\phi_n \qquad (3.18a)$$

$$\beta_{n+1}^* \, \phi^{n+1} = (1 - P_n^\dagger)\tilde{\Gamma}^\dagger \phi^n \qquad (3.18b)$$

where the projection operator P_n is written as

$$P_n = \sum_{j=1}^{n} |\phi_j\rangle\langle\phi^j| \qquad (3.19)$$

and the complex coefficient β_{n+1} is determined by the normalization condition $\langle \phi^{n+1} | \phi_{n+1} \rangle = 1$. It is easily shown that, in this new basis, $\tilde{\Gamma}$ may again be represented by a symmetric, but in general complex, tridiagonal matrix T with coefficients β_n as off-diagonal elements. This leads to the following three-term recursive relations:

$$\beta_{n+1}\phi_{n+1} = (\tilde{\Gamma} - \alpha_n)\phi_n - \beta_n\phi_{n-1} \qquad (3.20a)$$

$$\beta_{n+1}^* \, \phi^{n+1} = (\tilde{\Gamma} - \alpha_n^*)\phi^n - \beta_n^* \phi^{n-1} \qquad (3.20b)$$

with

$$\alpha_n = \langle \phi^n | \tilde{\Gamma} | \phi_n \rangle \qquad (3.21)$$

Since

$$\overline{J(\omega)/\delta A^* \delta B} = [(i\omega \, 1 + T \,)^{-1}]_{1,1} \qquad (3.22)$$

the continued fraction which appears at the right hand side of eq. (3.10) can

also be used for representing the frequency dependence of spectral densities calculated with operators which are not self-adjoint.

An alternative form for $J(\omega)$ is obtained from the solution of the eigenvalue problem for T

$$TQ = QA \tag{3.23}$$

Reference 29 reports on a modification of the QR algorithm for complex symmetric matrices which can be applied to this problem. The frequency dependence of $J(\omega)$ can then be explicitly written as follows:

$$\overline{J(\omega)/\delta A^* \delta B} = \sum_k Q_{1,k}^2/(i\omega + \lambda_k) \tag{3.24}$$

However this relation is more useful in displaying how the eigenvalues of the starting matrix enter into $J(\omega)$ than for practical purposes. In fact it is convenient to calculate $J(\omega)$ directly from the continued fraction without any matrix diagonalization.

It should be emphasized that the existence of the continued fraction representation of the spectral density is not assured if it is generated by means of a biorthonormal set of basis functions. It could happen, that the following scalar product [cf. eqs. (3.18)] vanishes:

$$\langle (1-P_n^\dagger)\bar{\Gamma}^\dagger\phi^n|(1-P_n)\bar{\Gamma}\phi_n\rangle = 0 \tag{3.25}$$

so that the normalization of ϕ^{n+1} and ϕ_{n+1} according to eq. (3.16) is no longer possible. When the Lanczos method is used with a self-adjoint $\bar{\Gamma}$ for generating orthogonal basis functions, a similar situation is found only if the right hand side of eq. (3.4) vanishes. In this case the operator $\bar{\Gamma}$ is factored with respect to the subspace spanned by functions $\phi_1, \phi_2, \ldots, \phi_n$, and the continued fraction truncated at the n-th term represents the spectral density completely. Of course, with biorthonormal basis functions, it would also be legitimate to truncate the continued fraction at the n-th term if $(1-P_n)\Gamma\phi_n$ or $(1-P_n^\dagger)\bar{\Gamma}^\dagger\phi^n$, or both vanish. However their scalar product could vanish simply because they are orthogonal, and in this case it would be impossible to derive a continued fraction representation of the spectral density. The spectral density of eq. (3.2) with $\langle\delta A|P_{eq}|\delta B\rangle=0$ constitutes an obvious example of such a situation. Normally, in the calculation of autocorrelation functions relevant to spectroscopic observables, such anomalous behavior is not found. It is however advisable to check the magnitude of the norm of the function in the scalar product of eq. (3.25), when it equals zero.

As in the simple case treated at the beginning of this chapter, the coefficients of the continued fraction are computed by the use of the recursive relations eqs. (3.20) with the ϕ_j's and ϕ^j's expanded in a given set of orthonormal basis functions f_j. Recalling the definition eq. (3.11) and eq. (3.13) for x_n, the recursive relations may be written as follows:

$$\beta_{n+1} x_{n+1} = (M - \alpha_n 1) x_n - \beta_n x_{n-1} \tag{3.26a}$$

$$\beta_{n+1}^* x^{n+1} = (M^+ - \alpha_n^* 1) x^n - \beta_n^* x^{n-1} \tag{3.26b}$$

where x_n is the column matrix constructed with the expansion coefficients of ϕ^n, and:

$$\alpha_n = (x^n)^\dagger M x_n \tag{3.27}$$

$$(x^{n+1})^\dagger x_{n+1} = 1 \tag{3.28}$$

The computer implementation of these relations requires the storage of four
vectors, as well as two multiplications of a square matrix by a column matrix at
each iteration. The computational effort is nearly doubled with respect to the
Lanczos algorithm with orthonormal basis functions. There is however an
important exception with complex symmetric matrices M if the starting vectors
are complex conjugate. That is, for n=1, we let:

$$x_n^* = x^n \tag{3.29}$$

Then it is easily shown from eqs. (3.26) that eq. (3.29) will be valid for all
values of n, provided $M=M^\dagger$. Therefore, only the recursive relation (3.26a)
needs to be explicitly computed, and the normalization condition eq. (3.28)
becomes:

$$x_n^{Tr} x_n = 1 \tag{3.30}$$

This is equivalent to the implementation of equation (3.12) with a "Euclidean
form" of the scalar product, in spite of the complex number algebra for the
matrix operations. Equation (3.30) is equivalent to the pseudo-norm that we
have previously introduced [6]. It should be noted here that often problems
involving operators $\bar{\Gamma}$ which are not self-adjoint, such as the stochastic Liou-
ville operators considered in magnetic resonance experiments, can be described
by complex symmetric matrices if the basis functions f_j are properly chosen
[6,21].

If the time evolution operator $\bar{\Gamma}$ is not "symmetrized", then it will not, in
general, be possible to represent it by a complex-symmetric matrix, for which
eq. (3.29) is true, and methods based upon biorthonormal spaces, as outlined
above, become essential. This approach has been discussed in detail by Wassam
[30].

Many aspects of the general analysis of the factors influencing the computer
performance of the (real symmetric) Lanczos algorithm [3,4] can also be applied
to our type of problem. In particular the sparsity of the matrix is crucial in
determining the efficiency of the method from both the point of view of computer
time and memory needed. Usually the matrix representations of the time evolu-
tion operators considered in the previous chapter have few non-vanishing ele-
ments. Values around 10-20% are typical sparsities, but it can be as low as a
few percent. Moreover, in general, one finds that there is a decrease in the
relative number of non-zero elements when one increases the degrees of freedom
included in the time evolution operator $\bar{\Gamma}$. In other words, the efficiency of
the Lanczos algorithm is enhanced in problems with large-size matrices.

It should be emphasized that the application of the Lanczos algorithm considered
here differs from its standard use in numerical analysis, in terms of the quant-
ity to be computed. Normally the Lanczos algorithm is considered in the frame-
work of the calculation of eigenvalues, while we need the spectral density as a
function of frequency, which is well described by the continued fraction eq.
(3.10), (but see Sect. IV). Correspondingly the convergence of the numerical
method must be considered in a different manner. In particular we must evaluate
how, by increasing the number of steps of the Lanczos algorithm, i.e. the number
of terms of the continued fraction, the spectral lineshape $I(\omega)$ of eq. (2.12)
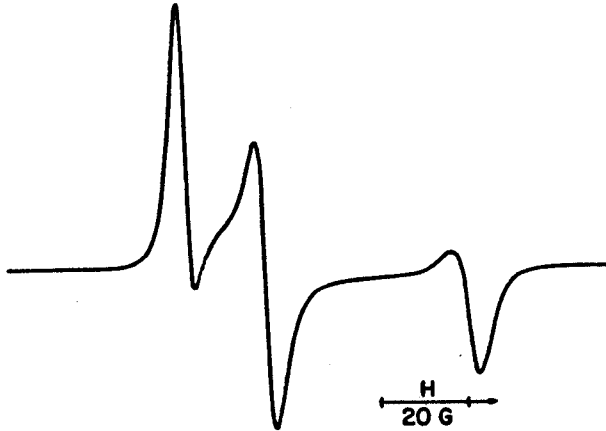approaches it converged form. In Figure 2 a typical ESR absorption spectrum is
displayed.

Figure 2
ESR absorption spectrum of a paramagnetic spin probe. The magnetic and motional
parameters are the same as case I in Table I of reference 6.

In numerical analysis, the convergence of the Lanczos algorithm with respect to
the individual eigenvalues has been considered in detail [31,32]. We are not
aware of any general criterion for the convergence of the spectral density. We
have found it convenient to use the following phenomenological definition of re-
lative error E_n for the spectral lineshape computed with n terms of the
continued fraction [6]:

$$E_n = \int_{-\infty}^{+\infty} d\omega \left| I_n(\omega) - I(\omega) \right| / \int_{-\infty}^{+\infty} d\omega \left| I(\omega) \right| \qquad (3.31)$$

Where $I(\omega)$ is the converged spectral lineshape. We think this definition of
E_n is a useful one, because it is a measure of the overall difference between
$I_n(\omega)$ and $I(\omega)$. Using this quantity, we can define the sufficient number of
steps n_s, as the smallest n which assures an error E_n less than the required
accuracy for the spectral lineshape. In general E_n decreases with n, but it
may not be strictly monotonic (see reference 6 for some typical trends). For an
accuracy $E_n = 10^{-4}$, n_s is found to be much less than the dimension N of the
matrix [6]. For large size problems, n_s is typically of the order of N/5 or
less. Of course this contributes to the overall efficiency of the Lanczos
algorithm by reducing the number of iterations.

In some problems the spectral density is dominated by only a few eigenvalues.
That is, in eq. (3.24) only a few of the weighting factors $Q_{1,k}^2$ are not
negligible. In these cases the Lanczos algorithm reproduces with comparable
accuracy the spectral lineshape and the dominant eigenvalues. There are other
situations, like the slow motional ESR spectrum displayed in Figure 2, where the
lineshape is a complicated function, which must be accounted for by a large col-
lection of eigenvalues. In such cases the Lanczos algorithm is more efficient
in reproducing the overall shape of $I(\omega)$ than in computing the eigenvalues [6].
Figure 3 illustrates this fact in displaying the computed eigenvalues of the ESR
problem considered in Fig. 2. The dots indicate the exact eigenvalues of the
starting matrix M which has a dimension equal to 42. The crosses represent the
16 eigenvalues of the tridiagonal matrix which approximate the lineshape to an
accuracy of 10^{-4}. From the Figure it is clear that there is no simple relation
between overall accuracy in the lineshape function and accuracy in the approxi-
mate eigenvalues. Most of them, in fact, cannot be simply associated on a one-
to-one basis with particular exact eigenvalues. Even when this is possible, the
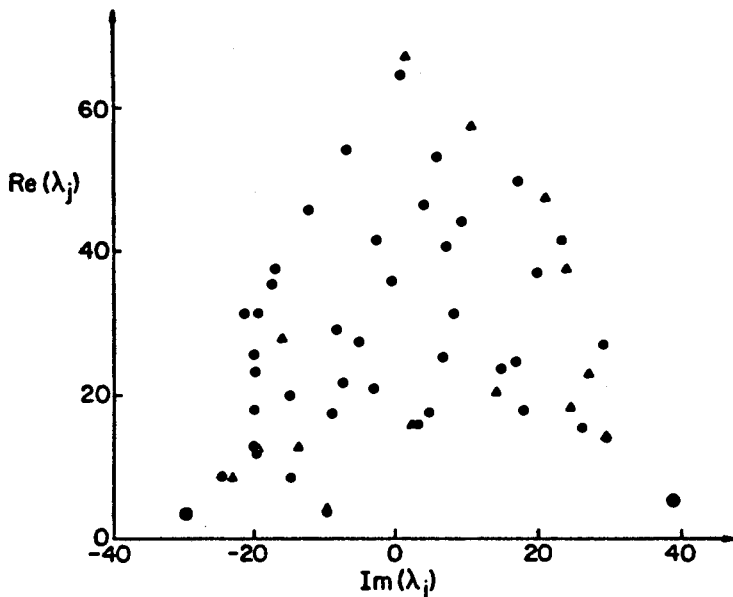error in the approximate eigenvalues is far greater than the accuracy of 10^{-4}

Figure 3
Distribution of the exact (dots) and approximate (△) eigenvalues relative
to the ESR spectrum displayed in Figure 2.

for the full spectrum (with the only exception being the eigenvalue having the
greatest imaginary part). We find therefore, that the Lanczos algorithm gener-
ates continued fractions which tend to optimize the overall shape of the
spectrum, rather than sets of eigenvalues. While at first such a statement
might appear contradictory, it is based on the fact that the spectral density is
usually dominated by the eigenvalues of small real part, and the Lanczos
algorithm is able to approximate them individually, or in providing an "average"
to a cluster of eigenvalues sufficient to represent the spectral density. A
qualitative justification of this behavior is implicit in the so-called method
of moments [23], since the subspaces generated by the Lanczos algorithm tend to
approximate the overall behavior of Γ by reproducing its first moments with
respect to the starting vectors.

We mention that in the types of problems we have been discussing, there have
almost never been significant effects due to round-off error, which, however, is
the main weakness of the Lanczos algorithm in the calculation of eigenvalues.
Qualitatively, this can be related to the same fact that the spectral density
converges much sooner than the corresponding eigenvalues, so that the loss of
orthogonality is not yet significant. It is known, in fact, that spurious
eigenvalues appear after a large enough number of Lanczos steps have been cal-
culated in order to obtain eigenvalues which are very close to their exact
values [32]. As noted above, this implies many more steps than are needed for
the convergence of the spectral densities. On the other hand, only a theory,
which is still lacking, that is specifically designed to analyze the convergence
of the spectral densities, could give a quantitative estimate of the effects of
the round-off error.

The last part of this chapter will be devoted to a discussion of the choice of
basis functions for representing the time evolution operator. First of all,
there is a truncation problem, since the functions $f_j(z)$, which form a

complete set to represent the Hilbert space associated with the functions of the
stochastic variables z, are in general infinite in number. In computer
calculations one can only handle finite matrices. Therefore one must truncate
the matrix M, i.e. one represents the operator Γ in a finite basis set of
functions f_1, f_2,..., f_N, under the hypothesis that the remaining functions
lead to negligible contributions. The truncation of the basis set leads to in-
correct features in the spectral density, while the computer calculation could
become exceedingly unwieldy with a too large basis set. In the absence of theo-
retical estimates of the error in $I(\omega)$ caused by the truncation, the convergence
must be verified directly from the computed results by comparing $I_N(\omega)$ obtain-
ed with increasing values of N. This is in the same spirit as the analysis of
convergence with respect to the number of steps of the Lanczos algorithm. Again
we can use eq. (3.29) as a measure of the truncation error. Clearly, as the
number of stochastic variables increases, the truncation problem becomes more
difficult and more time consuming.

Usually, in a given problem, one has a choice amongst different types of basis
functions. The best basis functions would be those which allow the most effi-
cient truncation, thus yielding the smallest matrix to be handled by means of
the Lanczos algorithm. There are no simple guidelines for such a choice, apart
from the obvious rule that all the symmetries of the time evolution operator
should be taken into account. (Other features in selecting a basis set include
the desirability to maximize the sparsity of the matrix and the ease of calcu-
lating the matrix elements). Only by experience with each particular class of
problems can one feel confident in selecting an optimal set of basis functions.

In some problems the desire for a minimal basis set suggests the use of non-
orthogonal functions. This is likely to happen when dealing with physical
systems characterized by mean potentials which confine the stochastic variables
 z around some stable states or conformations. Correspondingly, small ampli-
tude motions around the stable states (librations) and transitions amongst dif-
ferent states become the relevant dynamical processes. This type of problem is
commonly encountered in such fields of research as chemical kinetics in con-
densed phases [33-35] or in the study of conformational dynamics of chain mole-
cules or polymers [36-38]. From an analysis of the asymptotic behaviour of the
solutions of the diffusion equation, it has been shown that such problems can be
conveniently solved with non-orthoganal basis functions of the following type
[39-42]:

$$f_j(\ z\ )=g_j(\ z\ )\ P_{eq}(\ z\ )^{1/2} \qquad\qquad (3.32)$$

As long as one is able to mimic efficiently, by means of the functions g_j, the
fundamental processes occurring in hindered systems, very few elements of such a
basis set are needed in the calculation of the spectral density. The role
played by the factor $P^{1/2}$ in eq. (3.32) should be emphasized, since it
allows one to express $P^{1/2}_{eq}\hat{A}$ and $P^{1/2}_{eq}\hat{B}$ of eq. (3.2) simply as linear
combinations of properly chosen functions f_j's. On the other hand, with
orthonormal basis functions one must expand $P^{1/2}_{eq}$ in a large set of functions,
as a consequence of its sharp distribution around the stable state of the
system. (Alternatively one may introduce finite difference or finite element
methods to choose "localized" basis sets [43]).

Of course the implementation of the Lanczos algorithm must be changed when
passing from orthonormal to non-orthogonal basis functions. One may write the
matrix form for the spectral density eq. (3.2) by considering the representation
of the operator Γ and of the functions $P^{1/2}_{eq}$ A and $P^{1/2}_{eq}$ B in such a non-
orthogonal basis. One quickly sees that the calculation of the spectral density
is now closely related to the generalized eigenvalue problem $Ax=\lambda Bx$ [28].
Alternatively, we can start with the recursive relation of eq.(3.7) [or eq.

(3.18)] and implement them with non-orthogonal basis functions, in order to calculate the coefficients of the tridiagonal matrix. We shall discuss in detail this second route using the recursive relation eq. (3.7); i.e. for spectral densities of eq. (3.2) characterized by A=B and a self-adjoint operator Γ. One finds that the matrix recursive relation eq. (3.12) continues to hold if the generic column matrix x_n represents the expansion coefficients of ψ_n on the non-orthogonal basis set according to eq. (3.13), and if the matrix M is implicitly defined by the following relation:

$$\bar{\Gamma}f_j = \sum_k M_{jk} f_k \qquad (3.33)$$

One does need to modify the normalization condition and the calculation of diagonal coefficients, according to the following relations:

$$y_n^\dagger x_n = 1 \qquad (3.34)$$

$$\alpha_n = y_n^\dagger M x_n \qquad (3.35)$$

where y_n is an auxiliary column matrix calculated from the normalization matrix S

$$S_{jk} = \langle f_j | f_k \rangle \qquad (3.36)$$

and the array x_n according to the equation:

$$y_n = S x_n \qquad (3.37)$$

The operations of the standard Lanczos algorithm are easily modified to the present case [39,42]. In particular, during an iterative cycle one must store three arrays to represent the vectors x_n, x_{n-1} and y_n. By comparison with the standard Lanczos algorithm, the storage needed is then increased by one square matrix (S) and one array (y_n), while the computational effort is increased by the multiplication of a square matrix by a column matrix at each step, because of the calculation of y_n from eq. (3.37). Therefore, the use of non-orthogonal basis functions is convenient only when it allows a considerable reduction of the size of the matrices. This is generally the case in physical problems characterized by strong hindering potentials [42].

Unlike the case with orthogonal functions, the effect of the truncation of the basis to the first N elements cannot be carried out simply by neglecting the elements of M outside the first NxN block. As a matter of fact, the use of a finite basis set which defines an N-dimensional subspace ϵ_N, is equivalent to considering in eq. (3.2) the function $P^{1/2}_{\epsilon_\beta} \delta A$ and the operator Γ projected onto ϵ_N according to the following projector P_N:

$$P_N = \sum_{j=1}^{N} |f_j\rangle (S^{-1})_{jk} \langle f_k| \qquad (3.38)$$

Correspondingly, in the recursive relation eq. (3.7), one must substitute the operator Γ, by its projected form Γ'.

$$\bar{\Gamma}' \equiv P_N \bar{\Gamma} P_N$$

and the matrix M is implicitly defined by the following equation:

$$P_N \bar{\Gamma} f_j = \sum_k M_{kj} f_k \qquad (3.40)$$

After substitution of the projection operator of eq. (3.38), one obtains:

$$\mathbf{M} = \mathbf{S}^{-1} \mathbf{R} \qquad\qquad (3.41)$$

with R constructed with the matrix elements of $\bar{r}$:

$$R_{jk} = \langle f_j | \bar{r} | f_k \rangle \qquad\qquad (3.42)$$

We note that eq. (3.41) indicates that the calculation of M is more complicated than for the case of orthonormal basis sets. There are several methods for the calculation of M. First M can be computed directly from eq. (3.41), but this would require a large amount of computation time because of the inversion of S. Secondly, as suggested by Jones and coworkers [44,45]; one can implement the recursive relation (3.12) by calculating at each step the array $S^{-1}Rx_n$ from the solution of the linear system of equations with Rx_n as known coefficients. Thirdly, in some diffusional problems, one can write $\bar{r}f_j$ as a linear combination of basis functions by considering explicitly the operator form of $\bar{r}$ [39,42]. Thus the elements of M are derived by projecting out, according to eq. (3.38), only those functions which do not belong to ϵ_N [42].

SUMMARY

We have, in this review, outlined how the Lanczos algorithm is capable of play-ing a significant role in the calculation of spectral densities that arise in the study of molecular dynamics. This is, in part, due to its computational value and also to its close relationship to important theoretical methods in statistical physics. We have pointed out that these problems can often be represented by complex symmetric matrices, and the generalization of the Lanczos algorithm to such matrices has been generally successful. Further work is clearly needed in establishing a better understanding of how the Lanczos algo-rithm effectively projects out a useful representation of the spectral densities with much less effort than is required to obtain a good set of eigenvalues.

As problems become more complicated, and the matrix representations become larger, there is concern for careful selection of basis vectors including effective means of "pruning" out unnecessary basis vectors. Also, problems due to accumulated round-off can become more serious. Thus efficient techniques for partial re-orthogonalization may be called for [4].

In systems with strong trapping potentials, the use of non-orthogonal functions looks promising. So far, however, the method has been tested only in cases where the spectral densities can still be readily calculated with the use of standard orthonormal basis functions [39,42]. The application to challenging problems dependent on several degrees of freedom requires a search for optimal basis functions. Otherwise, the approach is straightforward apply.

Although we have emphasized in this work the calculation of spectral densities, what we have said here generalizes very nicely to the analysis of time domain experiments on molecular dynamics. In the context of linear response theory, the Fourier transform of the spectral density (or frequency spectrum) is just the time correlation function (or time domain response). Thus, many modern time-domain experiments may be described by first calculating the spectral density by the above methods and then using FFT routines to obtain the associated correlation functions. This equivalence again emphasizes the role of the Lanczos algorithm in selecting out and approximately representing the eigenvalues of small real part, i.e. the slowly decaying components, which usually dominate the time-domain experiments.

There is, however, a special case of time domain experiments: viz. the spin echo (and its optical analogues). These experiments may be thought of, to a first approximation, as canceling out the effects of the imaginary parts of the eigen-

values that contribute to the time domain response and thereby to provide great sensitivity in the experiment to the real parts. Analysis of spin-echo spectroscopy by the Lanczos algorithm has met with some success [46,47], because, as noted above, the eigenvalues of small real part tend to dominate the experimental observations, and they are the ones that are at least roughly approximated by the Lanczos algorithm. However, further computational developments along this line would have to address how to obtain better estimates of these "smaller" eigenvalues by improvements on the basic Lanczos technique.

ACKNOWLEDGMENTS

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