

The spectral moments method

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 3125

(<http://iopscience.iop.org/0953-8984/4/12/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 11:35

Please note that [terms and conditions apply](#).

The spectral moments method

C Benoit, E Royer and G Poussigue

Groupe de Dynamique des Phases Condensées, UA CNRS 233, Université Montpellier II, Sciences et Techniques du Languedoc, Place E Bataillon, 34095 Montpellier Cédex 5, France

Received 30 May 1991, in final form 1 November 1991

Abstract. A systematic analysis of the spectral moments method is presented and developed to compute the response functions of very large harmonic systems. Convergence of the algorithms is discussed and solutions are proposed to improve the results obtained. New developments are proposed. They concern, on the one hand, the determination of the Green functions or correlation functions of the system, and the localization of eigenvectors and, on the other hand, the determination of the spectral density of very large homogeneous matrices by a very simple and powerful technique. These results are illustrated by several examples taken from the main subjects studied by the authors: conducting polymers, fractals and quasi-crystals. Then comparison with other methods is discussed.

1. Introduction

It is well known that, in physics, the resolution of many problems requires the determination of eigenvalues and eigenvectors of a matrix. For instance, in quantum mechanics, the energy levels and the wavefunctions are given by the eigenvalues and eigenfunctions of the matrix corresponding to the Hamiltonian operator; in mechanics, for harmonic systems, the frequencies and the amplitudes of vibrations are obtained from the eigenvalues and eigenvectors of the dynamical matrix. If the system is not ordered as a crystal, the matrices can be very large and the usual methods fail to determine these quantities.

In several publications, we have shown that the moments methods are a powerful tool for the study of the dynamical properties of solids. In this paper, after a brief review, we will present the different techniques we used to obtain either the response functions of the system, the correlation functions, or the spectral density. In conclusion, we compare this method to the recursive method, which is somewhat similar.

To investigate the properties of a system, we generally apply a harmonic perturbation. The response of the system is then characterized by a function of the frequency of the perturbation: it is either a generalized susceptibility (dielectric susceptibility, magnetic susceptibility, elastic constants, conductivity) or a differential scattering cross section.

It appeared of interest to calculate the moments of this response versus frequency (or energy transfer) directly from the Hamiltonian of the system. For instance, in magnetic resonance, the first and second moments of the imaginary part of the magnetic susceptibility are calculated (Abragam 1961). The great advantage comes from the

fact that moments are related to the trace of operators, which is independent of the representation, thus circumventing the insoluble problem of finding the eigenstates of the total Hamiltonian. The higher moments are rather complicated functions of the Hamiltonian and they are difficult to determine with this type of method. However, many applications have been developed concerning the study of optical spectra (F centre; Henry and Slichter 1968), atomic photoabsorption, electron-atom scattering, nuclear level density and photoeffect studies (Dalton *et al* 1979). In these problems, it is necessary to work with a finite subset of a complete discrete set of square integrable (L^2) functions to discretize the Hamiltonian of the system. Brownian motion and Markovian processes have also been studied by moments techniques in classical mechanics (Dupuis 1967, Scheunders and Naudts 1990).

In solid-state physics the moments methods have been developed by Cyrot-Lackmann (1967), Gaspard and Cyrot-Lackmann (1973), Lambin and Gaspard (1982), Turchi *et al* (1982) and Jurczek (1985) for studies of electronic properties. They used the continued fraction expansion of the density of states. Up to Jurczek, the difficulty was to determine exactly the values of the coefficients of the continued fraction. Jurczek (1985) found a very simple iterative method, which is identical to the Stieltjes (1884) and the Chebyshev (1858) algorithms. For harmonic solids, a moments method was used first by Montroll (1942) to calculate the density of one-phonon states. The method was improved by Blumstein and Wheeler (1973) and Wheeler *et al* (1974). However, few works concern the direct determination of the response functions of the system. Only Gordon (1968) considered the first moments of the Raman and infrared spectra molecular systems. In dynamics of condensed matter, the possibility to determine directly the response functions from the Hamiltonian was pointed out for the first time by Galtier and Benoit (1981). Four years ago we developed a method based on the moments techniques that permits one to calculate the physical properties of very large disordered systems. The aim of this paper is to present the mathematical and computing aspects of this method, which we have called the spectral moments method as we calculate the moments of the spectral response of the system. We report also new developments such as the calculation of correlation functions and the spectral density of the matrix. Finally, we will discuss the accuracy of our technique.

The first point to be mentioned is that, generally, for systems without any particular symmetry properties, it is necessary to determine all eigenvalues and all eigenvectors of the dynamical matrix A of the system for which we wish to calculate the physical properties: optical spectra, conductivity, scattering properties and so on. The second point concerns the experimental data. Usually the experimental results are smoothed by the apparatus function or by the sensitivity of the detector and so do not involve the exact mathematical value of all eigenvalues and eigenvectors, especially for very large systems.

The only information that we need to obtain, with the best accuracy, is the number of eigenvalues, with the exact physical activity, which are in a very small spectral interval. If we call λ , the i th eigenvalue of the matrix A , we are chiefly interested in the best determination of the function $d(u) du$, which gives the number dN of eigenvalues λ , between u and $u + du$. This function can be written

$$d(u) = \sum_i \delta(u - \lambda_i). \quad (1)$$

We consider here the system with finite order matrix, so that the number of λ , is bounded.

The direct determination of (1) for very large matrices is very difficult. If we are interested only in larger eigenvalues and their corresponding eigenvectors, power methods with deflation procedure can be used (Saad 1981). However, it should not be used to compute more than a few eigenvalues and eigenvectors. Other methods (Lanczos 1950, Saad 1980) are based on projection techniques, both orthogonal and oblique, onto Krylov subspaces, i.e. subspaces spanned by the iterates of the power method. The well known iterative procedure (Haydock *et al* 1972, Haydock 1980) developed in solid-state physics is an application of these general techniques. These methods give a projected spectral density. We discuss in the last part of this paper their relations with the spectral moments method.

In physics only few experiments provide the spectral density directly; rather, the experimental results are connected to the 'linear response' of the system, which is given by the function (Born and Huang 1956):

$$f(u) = \sum_j d_j^* c_j \delta(u - \lambda_j) \quad (2)$$

with

$$c_j = \sum_i q_i e_{ij} \quad (3)$$

and

$$d_j^* = \sum_i p_i^* e_{ij}^* \quad (4)$$

where q_i and p_i are coefficients that are supposedly known from the physical problem. Let us recall that we are concerned by dynamical properties; generally the response function should be more complicated. In (3) e_{ij} is the i th component of the j th eigenfunction of A :

$$\sum_i a_{ij} e_{ij} = \lambda_j e_{ij} \quad (5)$$

where the a_{ij} are the elements of matrix A . We will see that the determination of (2) is much easier than the calculation of (1) and, furthermore, with some improvements, allows one to compute with good accuracy the spectral density (1).

We now begin to develop the spectral moments method. Then we will show how it allows one to determine the correlation functions or the Green functions of the system and finally we will study the way to obtain the spectral density. We illustrate these various points with several examples.

2. Moments method

In this section we present the main results that are used in the moments techniques. The detailed proofs can be found in Stieltjes (1884, 1894), Wall (1948), Shohat and Tamarkin (1963), Akhiezer (1965), Jones and Thron (1980), Benoit (1987, 1989) and Benoit and Poussiguet (1989).

2.1. Stieltjes inversion formula

Let us consider a function $G(u)$ that is positive and not decreasing. If $G(u)$ is bounded and non-decreasing on the interval $-\beta < u < +\beta$, then $G(u)$ is determined, except for an additive constant, at all its points of continuity, by the formula

$$G(u) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \int_0^u \operatorname{Im} R(z) \, du \quad (6)$$

with $z = u + i\varepsilon$ and where

$$R(z) = \int_{-\infty}^{+\infty} \frac{dG(v)}{z - v}. \quad (7)$$

$R(z)$ is called the Stieltjes transform of $G(u)$ and converges absolutely and uniformly.

2.2. Generalized moments

Let us now consider a function $g(u)$ that is positive on an interval (a, b) . Following Stieltjes, it is always possible to determine a polynomial $Q_n(u)$ of given degree n with the conditions

$$\int_a^b g(u) Q_n(u) u^k \, du = 0 \quad (k = 0, 1, 2, \dots, n-1). \quad (8)$$

The polynomials $Q_n(u)$ obey the following recurrence law:

$$Q_{n+1}(u) = (u - a_{n+1}) Q_n(u) - b_n Q_{n-1}(u) \quad (9a)$$

with

$$Q_{-1}(u) = 0 \quad \text{and} \quad Q_0(u) = 1 \quad (9b)$$

and where

$$a_{n+1} = \bar{\nu}_{nn} / \nu_{nn} \quad (10)$$

and

$$b_n = \nu_{nn} / \nu_{n-1, n-1} \quad (11)$$

with

$$\nu_{nn} = \int_a^b g(u) Q_n(u) Q_n(u) \, du \quad (12)$$

and

$$\bar{\nu}_{nn} = \int_a^b g(u) Q_n(u) Q_n(u) u \, du. \quad (13)$$

The quantities ν_{nn} and $\bar{\nu}_{nn}$ are called generalized moments. We will see that these quantities can be determined directly from the elements of the matrix A .

2.3. Continued fractions

The function $R(z)$ defined in (7) can be developed as a continued fraction:

$$R(z) = \frac{1}{z - \alpha_1 - \frac{\beta_1}{z - \alpha_2 - \frac{\beta_2}{z - \alpha_3 - \dots}}} \quad (14)$$

It is well known that a continued fraction is a limit of a fraction of polynomials, and one obtains

$$R(z) = \lim_{n \rightarrow \infty} \frac{P_{n-1}(z)}{R_n(z)}. \quad (15)$$

It is possible to show that for a function $g(u)$ that is positive on an interval (a, b) , such that

$$g(u) = dG(u)/du \quad (16)$$

$$R_n(z) = Q_n(z) \quad (17)$$

so that

$$\alpha_n = a_n \quad \text{and} \quad \beta_n = b_n \quad \text{for all } n. \quad (18)$$

The detailed demonstrations of these statements have been summarized in Royer (1989). Equations (5)–(18) are the basis of the moments method.

3. Spectral moments method—response functions

3.1. General form

Let us now consider the special form of $f(u)$ given in equation (2) with $q_i = p_i$. Now $f(u)$ is a positive function $g(u)$ everywhere. From the equation:

$$\delta(x) = \lim_{\varepsilon \rightarrow 0_+} \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2} \quad (19)$$

we obtain

$$g(u) = \frac{dG(u)}{du} = \sum_j \lim_{\varepsilon \rightarrow 0_+} \frac{1}{\pi} c_j^* c_j \frac{\varepsilon}{(u - \lambda_j)^2 + \varepsilon^2} = -\frac{1}{\pi} \sum_j \lim_{\varepsilon \rightarrow 0_+} \text{Im} \frac{c_j^* c_j}{z - \lambda_j} \quad (20)$$

with $z = u + i\varepsilon$. Now if we substitute the form (2) (with $q_i = p_i$) directly in (7) with (16), we obtain

$$R(z) = \sum_j \frac{c_j^* c_j}{z - \lambda_j} \quad (21)$$

and with (20) and (21) we obtain

$$g(u) = -(1/\pi) \lim_{\varepsilon \rightarrow 0_+} \text{Im} R(z). \quad (22)$$

So the inversion relations (6) are easily demonstrated with this particular form (20) for $g(u)$.

Our aim is to work with a large but finite-order matrix. So the number of eigenvalues is finite and from (2)

$$g(u) = \sum_{j=1}^N c_j^* c_j \delta(u - \lambda_j) \quad (23)$$

where N is the order of the matrix. In this case the continued fraction is finite. This can be proved in the following manner. From (15) and (17) we know that

$$R(z) = \lim_{n \rightarrow \infty} \frac{P_{n-1}(z)}{Q_n(z)}. \quad (24)$$

Following Stieltjes (1884, 1894) the polynomial $Q_n(z)$ has n distinct roots, so that

$$Q_n(z) = \prod_{j=1}^n (z - z_j). \quad (25)$$

The roots of $P_{n-1}(z)$ being different from z_j , equation (24) can be developed in simple fractions

$$R(z) = \lim_{n \rightarrow \infty} \sum_{j=1}^n \frac{M_j}{(z - z_j)}. \quad (26)$$

Comparison with (21) where the summation is finite shows that $z_j = \lambda_j$ and $M_j = (c_j, c_j)$ (usual scalar product) and that the continued fraction is finite. However, it has been shown by Stieltjes that the roots of the polynomials $Q_n(z)$ are non-degenerate, and a problem appears if some eigenvalues λ_j are degenerate. Let us suppose that $\lambda_1 = \lambda_2$. Then (21) can be written as

$$R(z) = \frac{c_1^* c_1 + c_2^* c_2}{z - \lambda_1} + \sum_{j=3}^N \frac{c_j^* c_j}{z - \lambda_j}. \quad (27)$$

Comparison with (26) shows that now $R(z)$ presents $n - 1$ poles and $Q_n(z)$ must be of degree $(n - 1)$ ($= Q_{n-1}(z)$) with

$$M_1 = c_1^* c_1 + c_2^* c_2 \quad (28)$$

and

$$M_j = c_j^* c_j \quad j = 3, 4, \dots, N. \quad (29)$$

Now let us consider the situation where some coefficients c_j are equal to zero. The number of distinct terms in (21) decreases and from equations (26) and (27) the degree of the polynomials $Q_n(z)$ also decreases. So the number of non-zero generalized moments is equal to the number of distinct eigenvalues with non-zero c_j coefficients. This is an important result for the moments method.

In conclusion, the determination of the coefficients a_n and b_n ((10) and (11)) allows the exact calculation of the function $R(z)$ (14) with the help of (18) and the exact determination of $g(u)$ by equation (22). The coefficients a_n and b_n are determined with the help of the generalized moments ν_{nn} and $\bar{\nu}_{nn}$ ((12) and (13)). The problem consists of determining these coefficients without knowledge of the function $g(u)$, directly from the Hamiltonian or from the dynamical matrix.

3.2. Computing aspects

To compute the linear response (23) we substitute $g(u)$ from (23) into (12) and (13). Let us consider first the moment ν_{mn} . With the help of the closure and orthogonality relations

$$\sum_i e_{\mu i}^* e_{ij} = \delta_{\mu j} \quad (30)$$

$$\sum_j e_{\mu j}^* e_{ij} = \delta_{\mu i} \quad (31)$$

and the relations (3) and (5), one obtains

$$\nu_{mn} = \sum_{i,i',l} q_i^* [Q_n(A)]_{il} [Q_n(A)]_{li'} q_{i'}. \quad (32)$$

In the same way the moment $\bar{\nu}_{mn}$ will be given by

$$\bar{\nu}_{mn} = \sum_{i,i',k,l} q_i^* [Q_n(A)]_{ik} A_{kl} [Q_n(A)]_{li'} q_{i'}. \quad (33)$$

With $Q_0(A) = I$ (identity matrix), one obtains directly ν_{00} and $\bar{\nu}_{00}$ from (32) and (33) and from the relation (9), one obtains

$$Q_1(A) = (A - a_1 I) \quad (34)$$

and thus ν_{11} and $\bar{\nu}_{11}$ and so on.

In practice, we do not work with the matrices but with a vector $t^{(n)}$ such that

$$t_i^{(n)} = \sum_i [Q_n(A)]_{ii} q_i. \quad (35)$$

Taking into account the relation (9), one obtains the following recursion formula for the vectors $t^{(n)}$:

$$t^{(n+1)} = (A - a_{n+1} I)t^{(n)} - b_n I t^{(n-1)}. \quad (36)$$

The generalized moments are then given by

$$\nu_{mn} = (t^n, t^n) \quad (37)$$

and

$$\bar{\nu}_{mn} = (t^n, A t^n). \quad (38)$$

We only need to store two vectors to compute all the generalized moments. Furthermore, we use a special method of storage for the matrix, A , which is often sparse: the non-zero elements are stored in a vector, while two tables give information on the indices; the first one gives the column of the element while the second table indicates the total number of non-zero elements at the end of every line. Codes for vector and matrix, matrix and matrix and triple matrix products have been constructed using vectorial and parallel programming. In other respects we have seen that the number of moments will be equal to the number of non-zero terms with distinct eigenvalues in equation (23). In many physical problems, only a few eigenmodes have a non-zero coefficient: for instance, for the infrared absorption in MgF_2 crystal only four modes (of the $N \sim 10^{23}$ modes) are infrared-active. The computation of the a_n and b_n will stop exactly after the fourth moment, which means $b_4 = 0$.

In practice, a test is inserted and the computation stops when b_n is smaller than a given value ($\sim 10^{-4}$). Now, when we compute physical properties of strongly disordered

materials or the spectral density, all eigenmodes will contribute more or less and it should be necessary to compute all the moments. This is not possible and in practice we determine a finite number of moments. Let us show why a good result is obtained.

3.3. Jacobi matrix

From a_n and b_n we construct the matrix (Whitehead in Dalton et al 1979):

$$J = \begin{bmatrix} a_1 & b_1^{1/2} & 0 & \dots \\ b_1^{1/2} & a_2 & b_2^{1/2} & \dots \\ 0 & b_2^{1/2} & a_3 & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \tag{39}$$

which is the Jacobi matrix associated with the moments of the spectrum. This is a symmetrical tridiagonal matrix and the following relation holds for the minors of $zI - J$:

$$\Delta_{n+1} = (z - a_{n+1})\Delta_n - b_n\Delta_{n-1} \tag{40}$$

where Δ_n is a diagonal minor of order n of $zI - J$. This relation is exactly the recurrence law for the polynomials $Q_n(z)$. The response function is the spectral density of the Jacobi matrix.

Let us consider now the truncated Jacobi matrix J_t

$$J_t = \begin{bmatrix} a_1 & b_1^{1/2} & 0 & \dots & \dots \\ b_1^{1/2} & a_2 & \dots & \dots & \dots \\ 0 & \dots & \dots & b_{n_c-1}^{1/2} & \dots \\ \dots & \dots & b_{n_c-1}^{1/2} & a_{n_c} & \dots \end{bmatrix} \tag{41}$$

If

$$\mu_n = \int u^n g(u) du \tag{42}$$

are the moments of the response function, then it is easy to show that

$$\mu_n = [J^n]_{11} = [J_t^n]_{11} \tag{43}$$

Hence truncating the full Jacobi matrix to any order produces a solution such that its $2n - 1$ independent moments agree exactly with the first $2n - 1$ moments of the exact solution. This result is of utmost interest.

However, in many problems, a sharp truncation causes the appearance of sharp lines in the calculated spectrum (see illustrations of spectral density). So, even if the calculated spectrum is such that its first $2n - 1$ moments agree exactly with the first $2n - 1$ exact moments, it is necessary to study very carefully the truncation of the continued fraction to obtain a good solution.

3.4. Infinite tail

Let us call $R(z)$ the exact value obtained with the total N_p moments that we suppose are all known and $R^c(z)$ the value obtained with the n_c practically calculated moments. We

have seen that N_p can be different from the order N of the matrix ($N_p \leq N$). One obtains after reduction of the continued fraction (14)

$$R(z) = P_{N_p-1}(z)/Q_{N_p}(z) \quad (44)$$

and for the computed value of $R^c(z)$,

$$R^c(z) = P_{n_c-1}(z)/Q_{n_c}(z). \quad (45)$$

It is possible to show that the following relation holds (Shohat and Tamarkin 1963):

$$P_{k-1}/Q_k = P_{k-2}/Q_{k-1} + b_1 \dots b_{k-1}/Q_{k-1}Q_k. \quad (46)$$

Using (44), (45) and (46) one obtains with $n_c < N_p$

$$R(z) = R^c(z) + \sum_{i=1}^{N_p-n_c} \frac{b_1 \dots b_{N_p-i}}{Q_{N_p-i}(z)Q_{N_p-i+1}(z)}. \quad (47)$$

The second term on the right-hand side of relation (47) represents the 'error' that is made when we cut the continued fraction. To decrease this error, a function $\varphi(z)$ is introduced that represents the effect of the cut tail (often called infinite tail in the limit $N \rightarrow \infty$); $\varphi(z)$ is given by

$$\varphi(z) = \frac{b_{n_c}}{z - a_{n_c+1} - \frac{b_{n_c+1}}{z - a_{n_c+2} - \frac{b_{n_c+2}}{z - a_{n_c+3} \dots - \frac{b_{N_p-1}}{z - a_{N_p}}}}} = \frac{P_{N_p-n_c-1}^\varphi(z)}{Q_{N_p-n_c}^\varphi(z)} \quad (48)$$

and is unknown. Now if we conjecture a form for $\varphi(z)$, one obtains for the calculated value of $R^c(z)$ after reduction:

$$R^c(z) = \frac{P_{n_c-1}(z) - P_{n_c-2}(z)\varphi(z)}{Q_{n_c}(z) - Q_{n_c-1}(z)\varphi(z)}. \quad (49)$$

As we shall see later, the choice of the form of the function $\varphi(z)$ is not trivial.

The problem of the convergence of continued fractions has been studied at length (Wall 1948). We report here the main results. For a fixed z ($\text{Im } z > 0$) the relation (49) maps the real axis of $\varphi(z)$ into the circumference of a certain circle $C_n(z)$ situated in the lower half-plane $\text{Im } R(z) < 0$ in such a way that the points of the half-plane $\text{Im } \varphi(z) < 0$ are mapped onto the interior of this circle. The circle $C_n(z)$ decreases, as n increases, in such a way that $C_n(z)$ is inside $C_{n-1}(z)$ and touches $C_n(z)$ from the inside. The radius of $C_n(z)$ is given by

$$r_{n_c}(z) = \rho_{n_c-1}/2\varepsilon \quad (50)$$

with

$$\frac{1}{\rho_{n_c-1}(z)} = \sum_{i=0}^{n_c-1} \frac{|P_i(z)|^2}{v_{ii}}. \quad (51)$$

It is possible to show that the general form for $\varphi(z)$ is

$$\varphi(z) = Az + c + \int_{-\infty}^{\infty} \frac{1+tz}{z-t} da(t) \quad (52)$$

where $a(t)$ is a bounded increasing function, A and c are real constants and $A \leq 0$.

The radius of $C_n(z)$ decreases when the imaginary part of z increases. However, if we increase ϵ , we decrease the resolution of spectral density or of the response function. Usually ϵ is taken as a constant. However, for some problems in mechanics or in self-similar systems it is interesting to plot the spectrum in $u^{1/2}$ or in $\log(u^{1/2})$. Then it is not possible to keep ϵ constant over all the spectrum and in practice ϵ is taken as a function of u , the width of the peak being a constant in linear (square root or log-log) plotting.

Some properties of the function $\varphi(z)$ can be derived directly by analysing the behaviour of the coefficients a_n and b_n :

(i) When we are dealing with the function (21), where the number of non-zero coefficients c_i is low, the form of $\varphi(z)$ is not very important if we compute a great number of moments.

(ii) Problem of the tail in solid-state physics has been studied (Gaspard and Cyrot-Lackmann 1973, Turchi et al 1982). In the presence of a gap the coefficients a_n and b_n exhibit undamped oscillations:

$$a_n = a + (-1)^n \delta a \quad \text{and} \quad b_n = b + (-1)^n \delta b \quad (n \text{ large}). \tag{53}$$

The tail $\varphi(z)$ is given by

$$\varphi(z) = -[\alpha \pm (\alpha^2 - 4\beta^+ \beta^- b^+)^{1/2}]/2\beta^- \tag{54}$$

with

$$\alpha = 2\delta b - \beta^+ \beta^- \quad \text{and} \quad \beta^\pm = z - a^\pm \tag{55}$$

and

$$a^\pm = a \pm \delta a \quad \text{and} \quad b^\pm = b \pm \delta b. \tag{56}$$

We used this type of tail in all the work done until now with the moments method. It is interesting to note that the effect of the tail depends strongly on the studied problem.

(iii) It is possible to generalize the method and to study the oscillations of the tail if the number of calculated moments is large enough. To do that we studied the Fourier components of the coefficients a_n and b_n . If these coefficients exhibit oscillations with the larger period m ,

$$a_n = a_{n+m} \quad \text{and} \quad b_n = b_{n+m} \tag{57}$$

then the tail will be given by

$$\varphi^{n,m}(z) = \frac{b_n}{z - a_{n+1} - \frac{b_{n+1}}{z - a_{n+2} - \dots - \frac{b_{n+m-1}}{z - a_{n+m} - \varphi^{n,m}(z)}}} \tag{58}$$

The solution of (58) is straightforward. Using the same relation as for (49) one obtains

$$\varphi^{n,m}(z) = [P_{m-1}^q(z) - P_{m-2}^q(z)\varphi^{n,m}]/[Q_m^q(z) - Q_{m-1}^q(z)\varphi^{n,m}] \tag{59}$$

with

$$\begin{aligned} P_{-1}^q(z) &= 0 & P_0^q(z) &= b_n \\ P_{s+1}^q(z) &= (z - a_{n-m+s+2})P_s^q(z) - b_{n-m+s+1}P_{s-1}^q(z) \end{aligned} \tag{60}$$

and

$$\begin{aligned}
 Q_{s+1}^q(z) &= 0 & Q_0^q(z) &= 1 \\
 Q_{s+1}^q(z) &= (z - a_{n-m+s+1})Q_s^q(z) - b_{n-m+s}Q_{s-1}^q(z).
 \end{aligned}
 \tag{61}$$

From (59) one obtains

$$\begin{aligned}
 \varphi^{n,m}(z) &= \{ [P_{m-2}^q(z) + Q_m^q(z) \pm \{ [P_{m-2}^q(z) + Q_m^q(z)]^2 \\
 &\quad - 4Q_{m-1}^q(z)P_{m-1}^q(z) \}^{1/2}] / 2Q_{m-1}^q(z) \}
 \end{aligned}
 \tag{62}$$

which generalizes the expression (54).

From the knowledge of the coefficients a_n and b_n ($n_c - m + 1 \leq n \leq n_c$) the polynomials and the tail of the continued fraction are computed.

Let us note that the infinite tail can be complex even with a real variable z . For instance with $a_n = a$ and $b_n = b$ whatever $n \geq n_c$ one obtains

$$\varphi(z) = \{ z - a \pm [(z - a)^2 - 4b]^{1/2} \} / 2
 \tag{63}$$

which is complex for

$$\operatorname{Re} z < 2\sqrt{b} - a
 \tag{64}$$

in the limit ε going to zero. Tail (63) gives an exact result.

There is no special reason for a particular periodic behaviour. For instance, in the quasi-periodic systems these coefficients follow a rather complicated law.

Illustrations will be discussed later principally for the determination of the spectral density. As we have already noted, the problem of the tail is generally less crucial in the determination of the response of the system.

Let us mention some other properties of the a_n , b_n , ν_{nm} and $\bar{\nu}_{nm}$:

(i) For a simple bounded and connected spectrum $0 < u < u_{\max}$ it is assumed that the coefficients a_n and b_n have definite limits such that (Turchi *et al* 1982)

$$a_n \rightarrow U_{\max}/2 \quad b_n \rightarrow (U_{\max}/4)^2.
 \tag{65}$$

(ii) Under change $u \rightarrow su$, the coefficients a_n , b_n , ν_{nm} and $\bar{\nu}_{nm}$ follow the scaling laws

$$\begin{aligned}
 a_n &\rightarrow sa_n & b_n &\rightarrow s^2b_n \\
 \nu_{nm} &\rightarrow s^{2n}\nu_{nm} & \bar{\nu}_{nm} &\rightarrow s^{2n+1}\bar{\nu}_{nm}.
 \end{aligned}
 \tag{66}$$

The change

$$a_n \rightarrow a_n + V
 \tag{67}$$

gives a general translation of the spectrum

$$u \rightarrow u - V.
 \tag{68}$$

The great advantage of the forms (54) or (62) of the tail is to respect the previous properties.

In conclusion of this analysis, the following method is used in the investigation of the spectrum:

(i) Choose the scaling factor s in (66) to calculate as many coefficients a_n and b_n as possible, taking into account the possibilities of the computer.

(ii) Analyse the general behaviour of the coefficients a_n and b_n , existence of a cut, divergence and so on.

(iii) Perform the Fourier analysis of the coefficients a_n and b_n to study the existence of the main periodicity.

(iv) Determine the radius of the circle $C_n(z)$ for all the spectrum and choose the best parameters.

(v) The function $R(z)$ is then computed with several types of function $\varphi(z)$.

We now report some examples of computation using these techniques.

3.5. Illustrations

3.5.1. *Fibonacci chain.* The first example concerns the Fibonacci chain (Benoit et al 1990). The matrix is tridiagonal and the values of the off-diagonal terms are obtained in the following procedure. The general off-diagonal terms can be generated from two basis elements A and B by an induction procedure as follows:

$$A \rightarrow B \quad B \rightarrow BA.$$

Stage 0 being A , the following sequence for off-diagonal terms is obtained:

$$A \rightarrow B \rightarrow BA \rightarrow BAB \rightarrow BABBA \rightarrow BABBBAB \rightarrow \dots$$

so that

$$a_{12} = B \quad a_{23} = A \quad a_{34} = B \quad a_{45} = B \quad \text{with } a_{ii'} = a_{i'i} \quad (69)$$

i.e. the off-diagonal elements follow a Fibonacci sequence. For the dynamical matrix the diagonal elements are given by

$$a_{ii} = -\sum_{i' \neq i} a_{ii'}. \quad (70)$$

This system has been widely studied and is a school example for the study of quasi-crystals. With this model it is possible to derive a response function (2) with the quantities $q_i(3)$ and $p_i(4)$ given by

$$q_i = e^{i(kr_i)} = p_i. \quad (71)$$

Physically k is the sound wavevector and r_i the position of the atom i . These quantities are assumed to be known. In such a hypothesis a peak must appear in $g(u)$ for a known

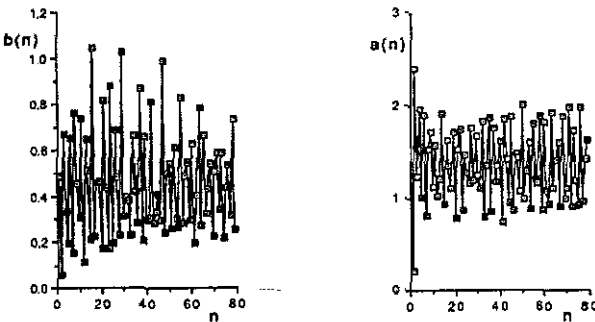


Figure 1. Values of the coefficients a_n and b_n for the Fibonacci chain. Order of the matrix = 5702 888.

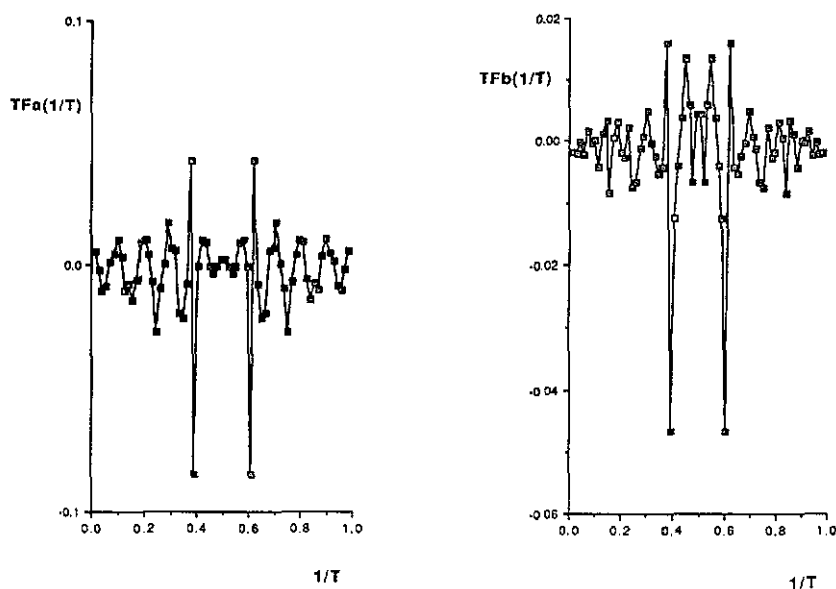


Figure 2. Fourier transform (TF) of the coefficients a_n and b_n for the Fibonacci chain. Order of the matrix = 5702 888.

value given by the theory as a function of A , B and k . The computation has been performed with $A = 7.83 \times 10^3$ dyne cm^{-1} , $B = A/2$, $k = 0.01$ Å (see Benoit *et al* 1990 for details). The values of the coefficients a_n and b_n are reported in figure 1. We note that b_2 is much lower than b_1 , showing that the spectrum will present few strong peaks. The Fourier analysis of the a_n and b_n is reported in figure 2. We note the presence of a pseudo-period close to 2.5. So we have chosen a value of $m = 5$ in equations (57)–(62). Radius of the circle convergence and response function are reported in figure 3.

We note that the radius is much smaller than the value of the response function. This result confirms the weak effect of the value of the infinite tail on the spectrum. The position of the low-frequency peak (upper curve in figure 3) agrees perfectly with the theoretical value (0.06 THz). Let us note that this value is in the very low part of the spectrum.

These results were obtained with a $5702\ 888 \times 5702\ 888$ matrix. The computing time on IBM 3090-600VF computer is 19 min 38.59 s. Some 334 Mb were needed for the computation of 80 generalized moments. Computing time is linear with the order of the matrix. However, the calculation shows that computation with a shorter chain ($N = 10\ 947$) gives good results.

In order to test the accuracy of the whole spectrum obtained (which is not reported here), we have calculated by direct integration the first moments of the spectrum. Let us recall that the form of this spectrum normally depends on the choice made for the tail. The results are reported in table 1 and show the excellent agreement obtained until the 10th moment. Direct computation of higher moments is not very accurate (lack of computing precision in integration).

These results prove two points: (i) for a spectrum with very few peaks, the results do not depend on the number of moments (upon a given value which is often small); (ii) the calculation is exact only for a Dirac spectrum ($\varepsilon \rightarrow 0$).

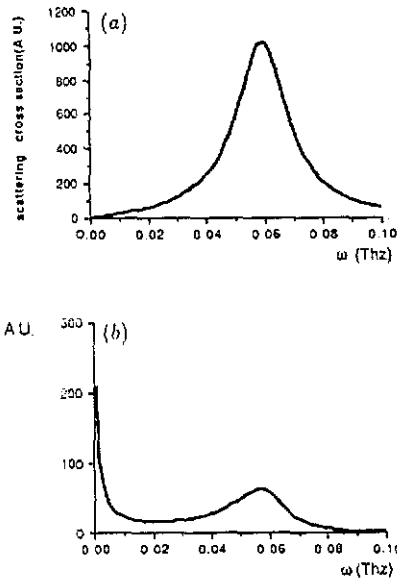


Figure 3. (a) Response function for the Fibonacci chain. Exact value of the position of the peak = 0.060 078 THz; calculated value = 0.060 08 THz. (b) Radius of the circle of convergence of the continued fraction for the Fibonacci chain.

Table 1. Test of the moments method (inelastic neutron scattering spectrum for a Fibonacci chain of 1598 atoms)^a.

ϵ	Number of 'exact' moments		
	$MQ = 60$	$MQ = 80$	$MQ = 100$
10^{-2}	2	2	2
10^{-4}	5	5	5
10^{-6}	7	7	7
10^{-8}	10	10	10

^a MQ is the number of calculated generalized moments; ϵ is the imaginary part of the complex variable z ; 'exact' moments are moments recalculated by integration that are in the vicinity of their initial value (less than 4%).

3.5.2. Polythiophene. Polythiophene is a conducting polymer after electrochemical doping. Its structure is stack of short and long linear chains composed of thienyl cycles joined head to tail. The equilibrium configuration and the interatomic potential in a chain are well determined (Poussigue and Benoit 1989). So it is possible to calculate the infrared response of such a compound within a simple model of atomic electric charges.

For a chain with 10 thienyl cycles we calculated the infrared spectrum for two polarizations: one along the chain axis Oz , and one along the perpendicular axis Ox in the configuration plane. Only the in-plane modes were active in such conditions. The dimension of the dynamical matrix was 144. So it was possible to obtain the infrared response either by exact diagonalization and determination of line strengths or by the spectral moments method. Figure 4 (corresponding to Oz polarization) shows the result: the spectra are identical. A similar result is obtained for Ox polarization.

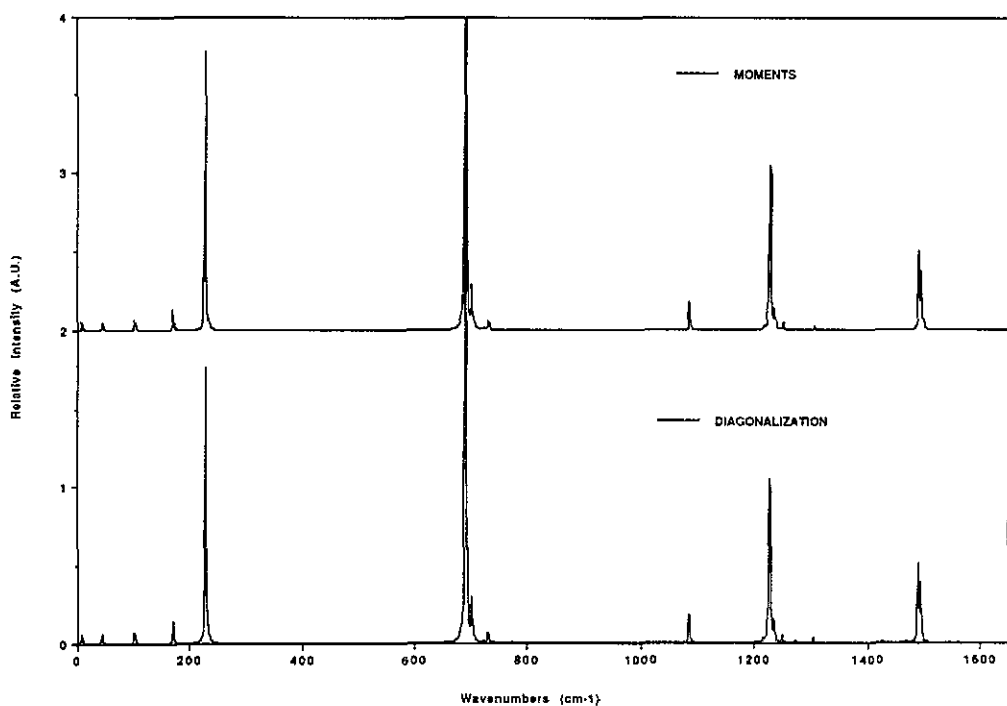


Figure 4. Calculated infrared spectrum for undoped polythiophene (polarization along Oz, axis of the chain) using the spectral moments method and by direct diagonalization.

These calculations were performed on a Macintosh II microcomputer. It was possible to perform the moments method up to chains with 100 thieryl cycles (dimension = 1444); one to two hundred moments were necessary to obtain a stable result. The moments computation time is linear with the dimension of the dynamical matrix and with the required number of moments. Generally the calculation of the spectrum from configuration, potential and charges takes no more than a few minutes. With this problem, we have computed up to 600 generalized moments without any divergence. In such a case the problem of the form of the infinite tail is completely unimportant.

All the results concerning calculated infrared and Raman spectra for doped and undoped polythiophene are developed in Poussiguet *et al* (1991).

Other examples of applications can also be found in Benoit (1987, 1989), Benoit and Poussiguet (1989) and Benoit *et al* (1992).

4. Correlation functions

4.1. General form—computing aspects

In physics, correlation functions or Green functions play an important role. For instance, these functions are correlated with the probability of finding an electron on the site i at time t if this electron was on site i' at time 0. In mechanics, these functions give a measure of the extent to which the displacement of the atom on site i is influenced by the fact that the atom on site i' suffered a displacement at time 0.

Let us define the Green matrix as

$$G(z) = (zI - A)^{-1}. \quad (72)$$

It can easily be shown that the imaginary part of the element ii' of (72) can be written

$$s_{ii'}(u) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \text{Im } G(z)_{ii'} = \sum_{j=1}^N e_{ij} e_{i'j}^* \delta(u - \lambda_j). \quad (73)$$

The structure of this equation is very similar to equation (2) with a particular choice for the value of the coefficients q_{i_0} and p_{i_0} (relations (3) and (4)):

$$q_{i_0} = \delta_{ii_0} \quad (i_0 = 1, 2, \dots, N) \quad (74)$$

for the right vector and

$$p_{i_0}^* = \delta_{i'i_0} \quad (i_0 = 1, 2, \dots, N) \quad (75)$$

for the left vector.

In (73) $s_{ii'}(u)$ is not a positive function everywhere and the spectral moments method does not work directly. So we define two positive functions $s_{++}(z)$ and $s_{--}(z)$, which are given by

$$s_{++}(u) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \text{Im } G(z)_{++} = \sum_{j=1}^N (e_{ij} + e_{i'j})(e_{jj}^* + e_{jj}^*) \delta(u - \lambda_j) \quad (76)$$

$$s_{--}(u) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \text{Im } G(z)_{--} = \sum_{j=1}^N (e_{ij} - e_{i'j})(e_{jj}^* - e_{jj}^*) \delta(u - \lambda_j). \quad (77)$$

These functions are positive and can be determined by a moments method. Then the Green functions are obtained directly from (76) and (77):

$$s(u) = [s_{++}(u) - s_{--}(u)]/4. \quad (78)$$

The method is equivalent to the spectral moments method with a special selection for the components of the $t^{(0)}$ vectors (see equation (35)).

In quantum mechanics, we work with the time-dependent position correlation function (Maradudin 1969):

$$G(i, i', t) = \langle \tilde{u}(i, t) \tilde{u}(i', 0) \rangle \quad (79)$$

with

$$\langle \tilde{O} \rangle = (1/Z) \text{Tr}(e^{-\beta H} \tilde{O})$$

where H is the Hamiltonian matrix, $\beta = 1/kT$, Z is the partition function and $u(i, t)$ is the displacement of the i th atom in the Heisenberg representation.

Evaluation of (79) is not possible as it requires knowledge of the exact eigenvalues and eigenvectors of the system. Using the imaginary part of the Fourier transform of (79) circumvents this difficulty:

$$G(i, i', \omega) = 2\pi\hbar [n(\omega) + 1] \sum_j \frac{e_{ij}}{\sqrt{m_i}} \frac{e_{i'j}}{\sqrt{m_{i'}}} \frac{1}{2\omega_j} [\delta(\omega - \omega_j) - \delta(\omega + \omega_j)] \quad (80)$$

where ω_j and e_{ij} are the frequency and the amplitude of mode j , $n(\omega)$ is the Boltzmann

factor and m_i is the mass of the atom i . Computation of $G(i, i', \omega)$ presents some difficulties and we worked with the following function:

$$\begin{aligned} \sigma(i, i', \omega) &= \sum_j \frac{e_{ij}}{\sqrt{m_i}} \frac{e_{i'j}}{\sqrt{m_{i'}}} \frac{1}{2\omega_j} [\delta(\omega - \omega_j) + \delta(\omega + \omega_j)] \\ &= \sum_j \frac{e_{ij}}{\sqrt{m_i}} \frac{e_{i'j}}{\sqrt{m_{i'}}} \delta(u - \lambda_j) = S(i, i', u) \end{aligned} \quad (81)$$

with $u = \omega^2$ and $\lambda_j = \omega_j^2$. This function is identically

$$\frac{1}{2\pi\hbar[n(\omega) + 1]} G(i, i', \omega)$$

for $\omega > 0$, symmetrical and independent of the temperature. It can be shown that, with $z = u + i\varepsilon$,

$$S(i, i', u) = - (1/\pi) \lim_{\varepsilon \rightarrow 0^+} g(i, i', z) \quad (82)$$

where the elements of $g(i, i', z)$ are given by $\langle i | (zI - A)^{-1} | i' \rangle$ where A is the dynamical matrix; relation (82) is now identical to relation (73) and the method is the same as developed for (73).

4.2. Localization ratio

We observed that, for a given value of u , the function $s_{i'}(u)$ was proportional to the wavepacket amplitude of the modes centred on u . We used the relation (78) to calculate the ratio of the second and fourth moments of the spatial distribution of the amplitude. Let us define

$$\mu_{2,i}(u) = \sum_{i'} |S_{i'i}(u)| (r_i - r_{i'})^2 \quad (83)$$

$$\mu_{4,i}(u) = \sum_{i'} |S_{i'i}(u)| (r_i - r_{i'})^4. \quad (84)$$

Then the localization ratio is

$$P_i(u) = \mu_{4,i}(u) / \mu_{2,i}(u). \quad (85)$$

This ratio gave the magnitude of the extension for the modes that concern atom i . The modes are more localized the smaller the ratio (85).

4.3. Illustrations

4.3.1. Chain with solitons. We consider a linear chain with two solitons as defects. The dynamical matrix is then given by

$$a_{i,i+1} = - \{k_0 + (-1)^i k_1 \tanh[(i - l_1)/\xi] \tanh[(i - l_2)/\xi]\} \quad (86)$$

with

$$a_{i'i} = a_{i'i} \quad \text{and} \quad a_{ii} = - \sum_{i' \neq i} a_{i'i} \quad (87)$$

where $\xi = 5$ is the width parameter, $k_0 = 0.125$, $k_1 = 0.025$, $l_1 = N/4$ and $l_2 = 3N/4$ are the centres of solitons (Su *et al* 1980, Benoit 1987).

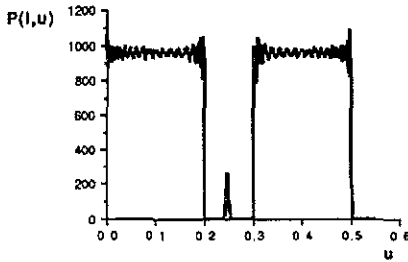


Figure 5. Localization ratio for a chain with solitons.

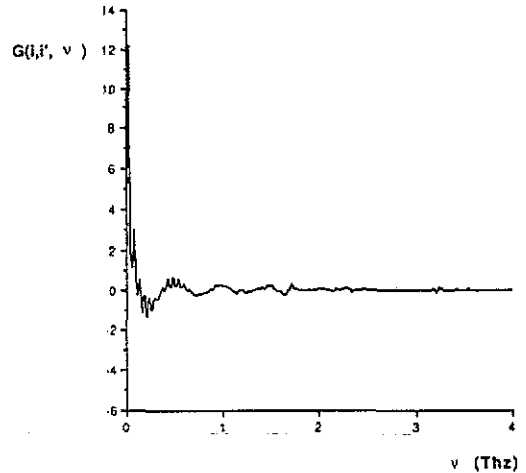


Figure 6. Imaginary part of the Fourier transform of the correlation function for the Fibonacci chain between two atoms i and i' . Atom i is at the centre of the chain and $i' = i + 20$.

The defects produce two localized modes centred on the solitons. The eigenvalues of these modes are exact for no interacting solitons at the centre of the spectral density. The envelope of these eigenmodes is centred on the defect j and behaves as

$$\varphi_i = \varphi_0 \operatorname{sech}[(i - l_j)/\xi]. \quad (88)$$

We report in figure 5 the localization ratio for this model computed from the correlation functions and from (85). We note that the modes are much localized in the centre of the gap. If one computes directly the localization ratio from (86) and (88), one obtains practically the same value. Let us remark that the exact value of ξ cannot be obtained from integration of (88) but from summation over the discrete sites of the lattice, using (88) for the computation of (83) and (84).

4.3.2. Fibonacci chain. We consider the same model as used for the illustration for the determination of the response function. We report in figure 6 the imaginary part of the Fourier transform of the correlation function between two atoms i and i' of a Fibonacci chain with 10 947 atoms. The atom i is an atom of the centre of the chain and $i' - i = 20$. This figure shows that the high-frequency vibrations are strongly localized.

4.3.3. Percolating networks. Percolating clusters were studied on a two-dimensional 1415×1415 square lattice above the percolation threshold $p_c (=0.593)$ for five values of the probability p (Royer et al 1992), where p is the occupation probability of the percolation network. We assume that atoms with mass m are placed at the sites of the lattice and are connected by springs. Displacements of the particles are represented by a scalar: for instance, the motion is in an orthogonal direction to the plane of the lattice.

Then the set of equations of motion for site i is given by

$$m\ddot{U}_i = -\sum_j k_{ij}U_j \quad (89)$$

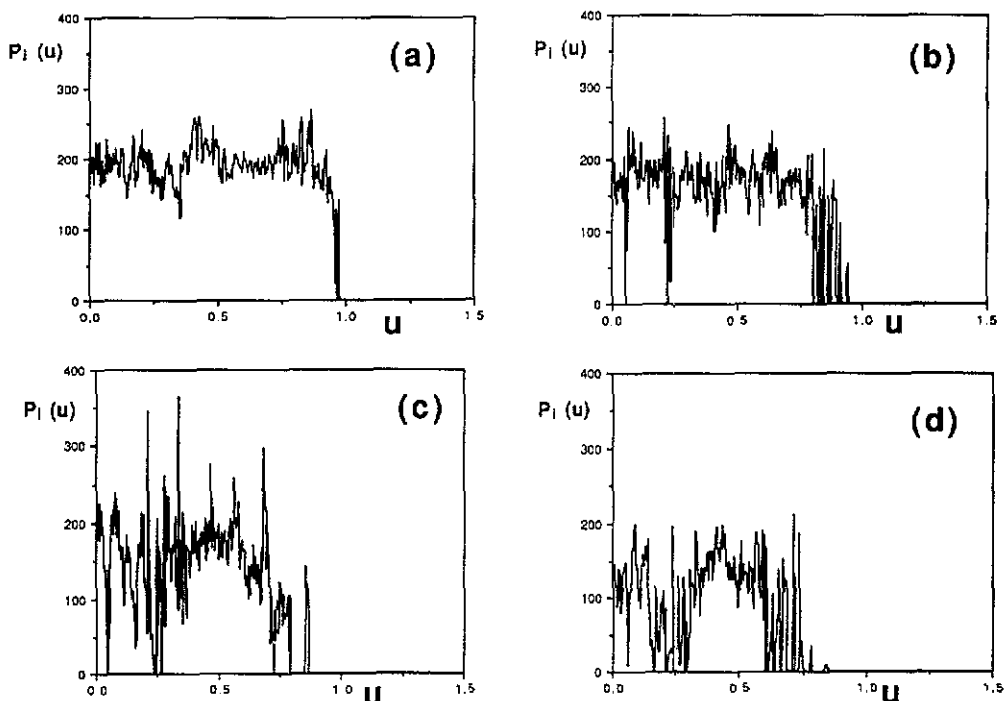


Figure 7. The localization ratio at different occupation probability of the percolation network for a square lattice 1415×1415 : (a) $p = 0.9$, (b) $p = 0.8$, (c) $p = 0.7$, (d) $p = 0.6$.

with

$$k_{ii} = - \sum_{j \neq i} k_{ij} \quad (90)$$

where j denotes the first neighbouring site of i , k_{ij} are force constants between the atoms i and j , which equal 0.125 if i and j are occupied, 0 otherwise. We report in figure 7 the localization ratio $P_i(u)$ with i chosen at the centre of the percolating cluster. From figure 7, we observe that, as p decreases to the percolation threshold, the high square frequency modes become more and more localized, rather quickly. Extended and localized modes are present at lowest frequencies.

5. Spectral density

We will show that the spectral method can be a very powerful tool for the computation of the spectral density of a very large matrix. We first recall the method that is usually used and is very close to the iterative method. We then present a new method based on the determination of a random response function.

From equation (73) after summation over i of the diagonal elements, one obtains with the help of (30) and (31)

$$-\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im Tr } G(z) = \sum_i s_{ii}(u) = \sum_{j=1}^N \delta(u - \lambda_j) = d(u) \quad (91)$$

and from the relations (12) and (13) with $d(u)$ instead of $g(u)$, the generalized moments

corresponding to the spectral density are

$$\nu_{nn} = \text{Tr}[Q_n^2(A)] \quad (92)$$

and

$$\bar{\nu}_{nn} = \text{Tr}[AQ_n^2(A)]. \quad (93)$$

Although the relations (92) and (93) are simpler than the relations (32) and (33), their use for computing the moments is more difficult because the determination of the trace of the n th power of a matrix A requires knowledge of the full matrix at the power $n - 1$. Even if A is a sparse matrix, A^{n-1} is certainly, for n large enough, a full matrix and the method cannot be applied for very large systems.

So, to obtain an approximate value of the spectral density for very large systems, two methods have been developed.

5.1. Local or projected spectral density

This method is already well known and is very close to the method developed from the Lanczos (1950) formalism. The relation (91) can be written

$$d(u) = \sum_i s_{ii}(u) = \sum_{i=1}^N \left(\sum_{j=1}^N e_{ij} e_{ji}^* \delta(u - \lambda_j) \right) \quad (94)$$

where $s_{ii}(u)$ is the local spectral density on the 'state' (or site) i . For a site i given, all the p_k and q_k are set to zero except for $k = i$ and now the relations (37) and (38) with the help of (36) can be used. The spectral density is obtained by making the summation over all sites of the local spectral density. However, it is not very interesting. Usually, the computation is made over a few sites that are of particular interest.

We present a new second method, which is much more practicable.

5.2. Random moments method

We develop now a method that can be used to determine the density of states (DOS) of non-periodic, harmonic systems. We consider now the relation (2) with $d_i = c_i$,

$$f(u) = \sum_i^N c_i^* c_i \delta(u - \lambda_i). \quad (95)$$

This relation can be written as

$$f(u) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \sum_{i,i'} q_i G(z)_{ii'} q_{i'}^*. \quad (96)$$

Now starting from (96), we consider a canonical ensemble of M identical systems with dimension N , and we study the following relation:

$$h(u) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \left[\text{Im} \left(\frac{1}{\mathcal{M}} \sum_{\alpha=1}^M \sum_{i,i'=1}^N q_i^\alpha G(z)_{ii'} q_{i'}^{\alpha*} \right) \right] \quad (97)$$

in the limit of M and N going to infinity. Here the q_i^α components are independent random variables distributed according to the continuous bounded probability density function $P(q_i^\alpha)$. Thus for all q_i^α , $P(q_i^\alpha) dq_i^\alpha$ is the probability that q_i^α lies in the range

$(q_i^\alpha, q_i^\alpha + dq_i^\alpha)$. $P(q)$ is identically zero except in a region $-0.5 < q < 0.5$. We investigate numerically the class for $P(q) = 1$. Then the following relation holds for N going to infinity:

$$\frac{1}{N} \sum_{i=1}^N q_i^\alpha q_i^\beta = \mathcal{A} \delta_{\alpha\beta} \quad (98)$$

where \mathcal{A} is a normalization constant, which is equal to $1/12$ here. The same rule holds also for the components of different systems when M goes to infinity:

$$\frac{1}{M} \sum_{\alpha=1}^M q_i^\alpha q_i^\alpha = \mathcal{A} \delta_{ii'}. \quad (99)$$

As the distribution is centred on zero, one obtains

$$\frac{1}{N} \sum_{i=1}^N q_i^\alpha = 0 \quad (100)$$

and

$$\frac{1}{N} \sum'_{i,i'=1}^N q_i^\alpha q_{i'}^\alpha = 0 \quad (101)$$

where the prime indicates that i and i' are taken different.

Starting from these remarks, we will show that it is possible to determine very simply the density of states by a moments technique. With the help of relation (99), (97) becomes

$$h(u) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0_+} \left[\text{Im} \left(\sum_{i,i'=1}^N G(z)_{ii'} \delta_{ii'} \right) \right] = d(u) \quad (102)$$

which is exactly the density of states of the system in the limit $M \rightarrow \infty$.

However, the direct use of relation (97) is not easy, as we have to make the summation over a great number of systems. But we will see that, if the system is very large and homogeneous enough, it is not necessary to sum over many systems of the canonical ensemble.

Usually the elements of the dynamic matrix A take few different values: for instance in the scalar model of the Sierpinski gasket, we have only two different values (with the diagonal elements); in polyacetylene, with long-range forces, there are only 10 different matrix elements. In the same way, we can assume that the Green matrix is somewhat homogeneous. So we call μ the set of elements of G having the same value. The set μ contains N_μ elements

$$G_{i\mu i'}(z) = C_\mu(z) \quad (103)$$

which are all equal.

We calculate the relation (97) by taking into account that elements of the same set are equal. One obtains

$$h(u) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0_+} \left\{ \text{Im} \left[\frac{1}{\mathcal{A}M} \sum_{\alpha=1}^M \sum_{\mu} \left(G_{i\mu i'}(z) \sum_{i\mu}^{N_\mu} q_{i\mu}^{\alpha 2} \right) \right] \right\} \\ - \frac{1}{\pi} \lim_{\varepsilon \rightarrow 0_+} \left\{ \text{Im} \left[\frac{1}{\mathcal{A}M} \sum_{\alpha=1}^M \sum'_{\mu} \left(G_{i\mu i'}(z) \sum_{i\mu i'}^{N_\mu} q_{i\mu}^\alpha q_{i'}^\alpha \right) \right] \right\} \quad (104)$$

where we have separated the summation over diagonal and off-diagonal elements. If the values of N_μ are large enough, the relations (98)–(101) hold for every subset μ . Taking into account (101), we see that the second part of (104) goes to zero. The first part gives, taking into account (99),

$$h(u) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \left[\text{Im} \left(\frac{1}{AM} \sum_{\alpha=1}^M \sum_{\mu} [G_{i,\mu}(z) \mathcal{A} N_{\mu}] \right) \right] \quad (105)$$

and the summation over μ gives the trace of $G(z)$ (equation (96)). So one obtains again $h(u) \rightarrow d(u)$ for homogeneous systems where the matrix is large enough. Now the computation is made over only one or a few systems of the canonical set depending on the structure and dimension of the matrix. The method consists of calculating the relation

$$d(u) = -\frac{1}{\pi} \frac{1}{AM} \sum_{\alpha=1}^M \lim_{\epsilon \rightarrow 0^+} [\text{Im} G^{\alpha}(z)] \quad (106)$$

with

$$G^{\alpha}(z) = \sum_{i,i'=1}^N q_i^{\alpha} G(z)_{ii'} q_i^{\alpha}. \quad (107)$$

For every system of the statistical ensemble one uses the method developed for the computing of the response function and takes the average over calculated spectrum. For a very large homogeneous matrix, it is often sufficient to work with only one system.

To test the accuracy of the method, we calculated the fluctuation ratio \bar{R} over every point of the spectrum of the Fibonacci chain.

For a value u_i of the spectrum we determined

$$\bar{g}(u_i) = \frac{1}{M} \sum_{\alpha=1}^M g^{\alpha}(u_i) \quad (108)$$

and we obtained the mean fluctuation ratio over all the spectrum from the relation

$$\bar{R} = \frac{1}{N_s} \sum_{i=1}^{N_s} \left(\frac{1}{M} \sum_{\alpha=1}^M [g^{\alpha}(u_i) - \bar{g}(u_i)]^2 \right)^{1/2} \quad (109)$$

where N_s is the number of calculated points. Results are reported in figure 8. We note that, as expected for a very large matrix, few runs are necessary to obtain a good spectral density.

5.3. Illustrations

5.3.1. Polythiophene. We report in figure 9 the determination of the spectral density performed by direct diagonalization, by a statistical average over random sites of the local spectral density and by random moments method. The average is taken over 10 random sites for the local spectral density method and over 10 systems for the random moments method.

The results are shown in figure 9, where the density obtained by diagonalization is a full curve and the density obtained by the moments method with local charges is a broken curve. The peaks have the same wavenumbers but there are a few discrepancies between the magnitude of the peaks. This is due to the fact that 10 choices of a site do not represent

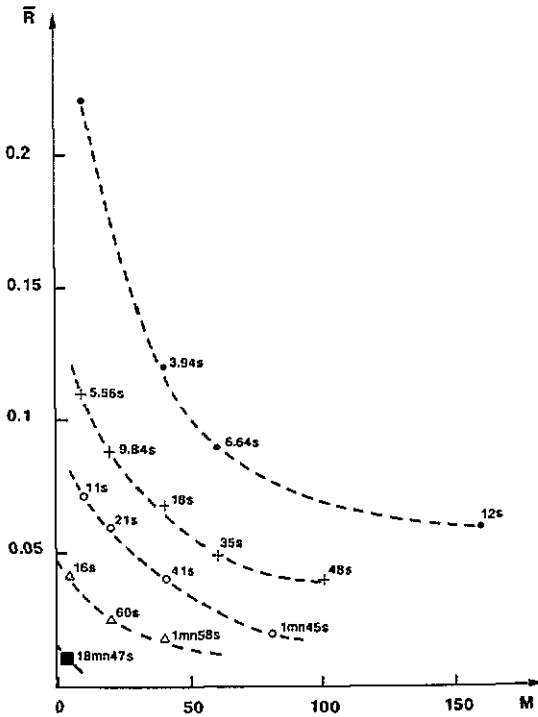


Figure 8. Mean fluctuation ratio over all the spectrum as a function of the number M of systems for several sizes of the matrix: 35 (●), 611 (+), 4182 (○), 10947 (△) and 2178310 (■) atoms in the Fibonacci chain. The CPU time is reported for each point.

perfectly the whole problem with a rather complicated dynamical matrix. The density obtained by the moments method with random charges is a dotted curve. Although the matrix is not very homogeneous and its rank is small, the result is not bad and much better than with the local charges.

5.3.2. Percolation network. To test the accuracy of the random moments method, we first compared the result of the moments technique developed here for the spectral density and the exact result obtained for a regular square lattice. We worked on a 1415×1415 lattice, and general agreement with the exact result is obtained for $u > 0.03$ ($u_{\max} = 1$) (figure 10) with only $M = 1$ (equation (106)).

To determine the behaviour of the spectral density in the very low-frequency region we plotted it on a log-log scale. With the biperiodicity for the infinite tail (54), one obtains the result reported in figure 10, which is wrong. The radius of the circle of convergence is reported in figure 11 for several values of the number of moments. We note that the radius decreases rapidly with the number of moments. However, it diverges strongly in the low-frequency region. This region needs to be studied carefully. The coefficients a_n , b_n and their Fourier transforms are reported in figure 12. The results show that a nearly 4-period exists in this system. The spectral density obtained with the period $m = 4$, equation (62), is shown in figure 13. The result agrees very well with the exact value for all the spectrum. For the percolating network for $p = 0.6$, for instance, analysis of the data shows that the coefficients a_n and b_n present a 12-period.

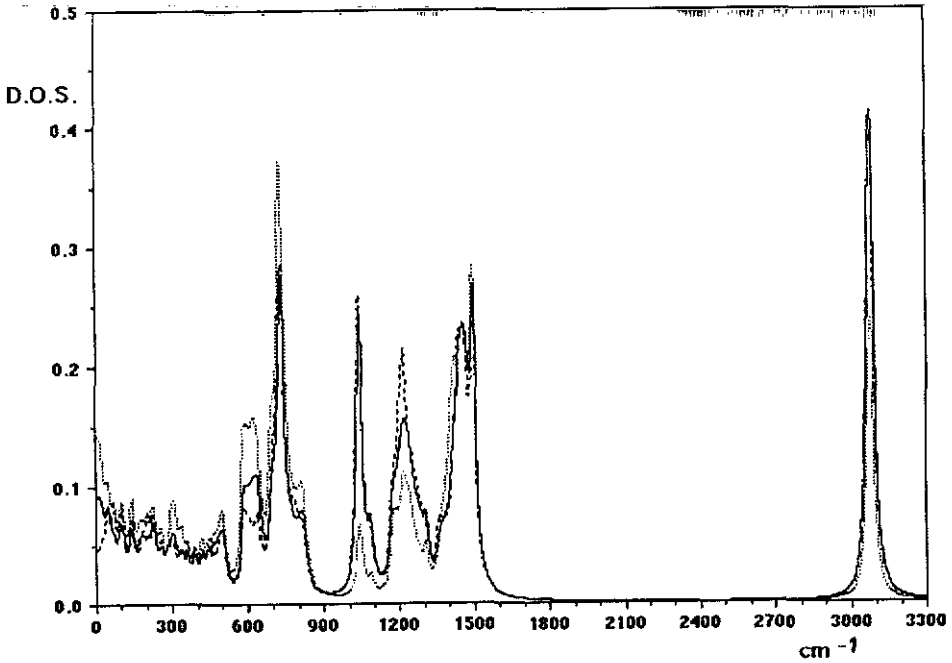


Figure 9. Spectral density of polythiophene chain calculated either by direct diagonalization (full curve), or using the spectral moments method with random charges (dotted curve) and with local charges (broken curve).

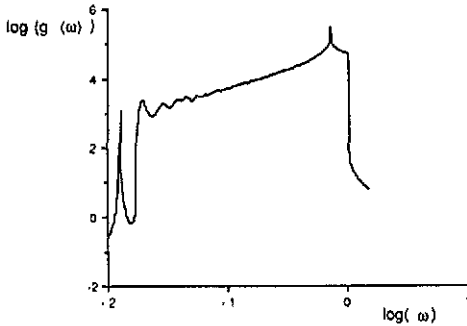


Figure 10. Log-log plot of the spectral density of square lattice $p = 1$ with 180 generalized moments. Infinite tail with biperiodicity and $\epsilon = 0.001$.

The computations were performed from probability $p = p_c$ to $p = 1$, on the same lattice. The size of the percolating clusters that corresponds with this model to the range of the dynamic matrix and the computing time are reported below:

p	Size	CPU time	
		(1)	(2)
0.6	904 068	39 min 49 s	6 min 32 s
0.7	1378 975	10 min 03 s	7 min 15 s
0.8	1599 431	5 min 41 s	7 min 56 s
0.9	1802 855	3 min 29 s	8 min 41 s
1	2002 225		9 min 21 s

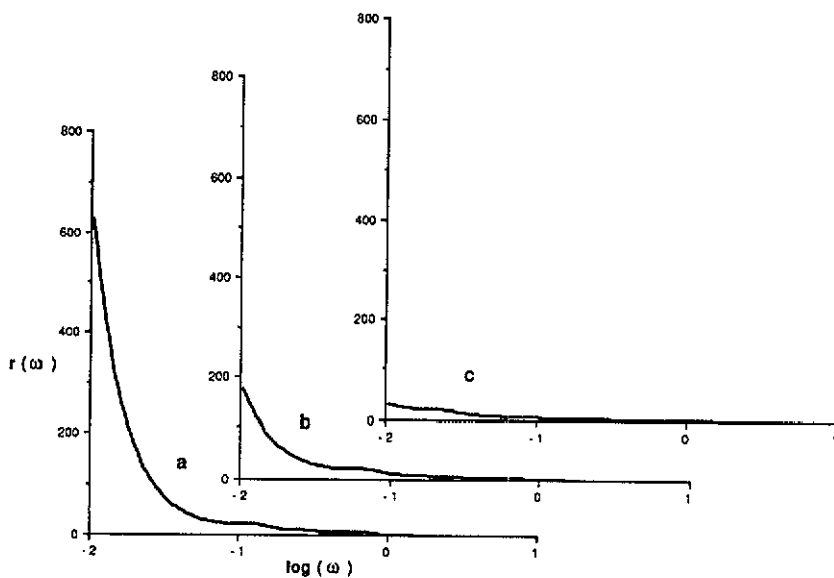


Figure 11. The radius of the circle of convergence of a square lattice for several values of the number of moments and $\varepsilon = 0.01$: (a) 10 moments, (b) 20 moments, (c) 60 moments.

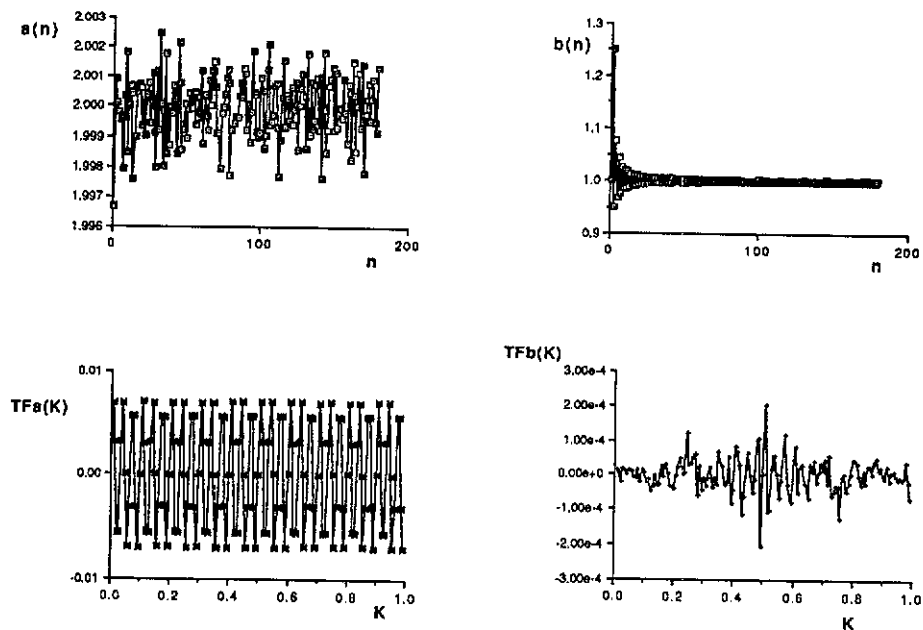


Figure 12. Values of the coefficients a_n and b_n and their Fourier transforms (TF) for the square lattice ($p = 1$).

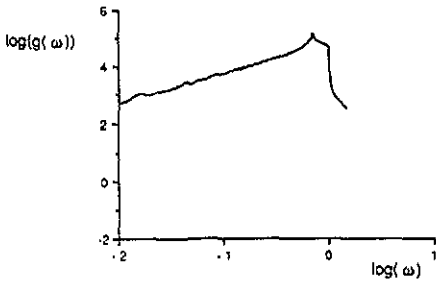


Figure 13. Log-log plot of the spectral density of square lattice ($p = 1$) with 170 generalized moments. Infinite tail with 4-periodicity and $\varepsilon = 0.01$.

CPU time (1) is the time to find the percolating cluster and construct the dynamical matrix; CPU time (2) is the time to compute the DOS of the percolating cluster. At $p = 1$, a unique program is followed, since all the sites of the lattice form the cluster. It is the first time that such large clusters have been studied in dynamics.

6. Comparison with other methods and conclusions

To compute the properties of general systems without particular symmetry or special dimension, most codes allow one to do the following:

(i) To compute eigenvalues and eigenvectors of matrices with a rank of about 1000–2000 taking into account their structure with a classical method (Gaussian elimination) with long computing time (Quiming Li *et al* 1990).

(ii) To work with matrices of rank of about 100 000 with deflation techniques. However, only smaller (or larger) eigenvalues and corresponding eigenvectors can be calculated with these methods (Saad 1980, 1981).

(iii) To determine the spectral density of systems with matrices of rank 300 000 with the resonance method: a random force is applied to atoms and the spectral density is obtained directly from the mean energy of atoms (Williams and Maris 1985). This method is a method at a given frequency, which means that the probability of missing an important mode is not negligible.

Let us mention also the negative eigenvalues method, which permits one to calculate the spectral density of a large system (2000–3000 and perhaps more; Dean 1960). However, this method is not very practicable in the determination of eigenvectors. The last method is the Lanczos method or its solid-state application, the recursive method, which allowed the determination of the projected spectral density of large systems (Lanczos 1950, Haydock *et al* 1972, Haydock 1980). This method is equivalent to the moments method in its simplest form. Consider a matrix A and a vector v_1 . We form new vectors as follows (Arnoldi's method in Saad (1980)): choose v_1 of norm 1 and iterate for $j = 1, N$

$$h_{ij} = (Av_i, v_j) \quad i = 1, 2, 3, \dots, j \quad w_j = Av_j - \sum_{i=1}^j h_{ij}v_i \quad (110)$$

$$h_{j+1,j} = |w_j| \quad v_{j+1} = (1/h_{j+1,j})w_j.$$

In the basis of vs the matrix A is the Jacobi matrix (39) with $h_{nn} = a_n$ and

$h_{n,n+1} = b_n^{1/2}$. The iteration (110) is equivalent to (36) with a different norm for the vector.

However, in the spectral moments method we are often dealing with more general problems than the simple determination of the spectral density. For example, the diffusion of light is related to the following expression (Benoit 1987, Benoit *et al* 1992):

$$\begin{aligned} I_{\alpha\gamma\beta\lambda} &= \sum_j a_{\alpha\gamma}^*(j) a_{\beta\lambda}(j) \frac{1}{2\omega_j} [\delta(\omega - \omega_j) + \delta(\omega + \omega_j)] \\ &= \sum_j \chi_{\alpha\gamma}^*(j) \chi_{\beta\lambda}(j) \delta(u - \lambda_j) \end{aligned} \quad (111)$$

with ($q = 0$)

$$a_{\alpha\gamma}(j) = \sum_i \frac{\chi_{\alpha\gamma,i}}{\sqrt{m_i}} e_{ji} \exp(iq \cdot r_i) \quad (112)$$

where the $\chi_{\alpha\beta,i}$ are the local susceptibility tensor for the atom i with mass m_i .

The relation (111) is identical to equation (2) and the generalized moments are now given, for $\alpha, \beta, \gamma, \lambda$ fixed, by

$$\nu_{nn} = \sum_{i,i',l} \chi_{\alpha\gamma,i}^* [Q_n(A)]_{il} [Q_n(A)]_{l'i'} \chi_{\beta\lambda,i'} \quad (113)$$

In the same way the moments $\bar{\nu}_{nm}$ are given by

$$\bar{\nu}_{nn} = \sum_{i,i',l,k} \chi_{\alpha\gamma,i}^* [Q_n(A)]_{il} A_{lk} [Q_n(A)]_{k'i'} \chi_{\beta\lambda,i'} \quad (114)$$

It is clear that we cannot use directly the recurrence relations (110); as the right and left coefficients are different, the moments method and simple recursive method are no longer equivalent. However, there is no doubt that after some modifications in the Lanczos iterations it should also be possible to compute the Raman spectra.

Another example of a problem that cannot be treated by a direct recursive method is the determination of the combined frequency distribution or the second-order spectra where one determines the generalized moments from a bilinear combination of usual moments (42) (Benoit 1987). A great advantage of the moments is that they are linear with the density of states. Furthermore, we have seen that, for quantum systems, the moments of the response can be obtained directly from the Hamiltonian. It is evident that use of the method described in this paper will give interesting results in these fields of research.

Acknowledgments

We thank M Durand and S Carta from IBM France, and G Urbach, M Battle and G Gil from Centre National Universitaire Sud de Calcul (CNUSC-Montpellier) for their great help on the computing aspects of this work.

This work was supported by IBM France and the Centre National Universitaire Sud de Calcul (Ministère de l'Education Nationale) contract C3NI (High Performance Computing).

References

- Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Clarendon)
- Akhieser N 1965 *The Classical Moment Problem* (Edinburgh: Oliver and Boyd)
- Benoit C 1987 *J. Phys. C: Solid State Phys.* **20** 765
- 1989 *J. Phys.: Condens. Matter* **1** 335
- Benoit C and Poussigie G 1989 *High Performance Computing* ed J L Delaye and E Gelenbe (Amsterdam: North Holland) p 347
- Benoit C, Poussigie G and Assaf A 1992 *J. Phys.: Condens. Matter* **4** 3153
- Benoit C, Poussigie G and Azougarh A 1990 *J. Phys.: Condens. Matter* **2** 2519
- Blumstein C and Wheeler J C 1973 *Phys. Rev. B* **8** 1764
- Born M and Huang K 1956 *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon)
- Chebyshev P L 1858 *J. Math., 2nd Ser.* **III** 289
- Cyrot-Lackmann F 1967 *Adv. Phys.* **16** 393
- Dalton B J, Grimes S M, Vary J P and Williams S A (ed) 1979 *Theory and Applications of Moment Methods in Many Fermion Systems* (New York: Plenum)
- Dean P 1960 *Proc. R. Soc. A* **254** 507
- Dupuis M 1967 *Prog. Theor. Phys.* **37** 502
- Galtier M and Benoit C 1981 *Phys. Status Solidi b* **105** K61
- Gaspard J P and Cyrot-Lackmann F 1973 *J. Phys. C: Solid State Phys.* **6** 3077
- Gordon R 1968 *J. Math. Phys.* **9** 655
- Haydock R 1980 *Solid State Physics* vol 35, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic)
- Haydock R, Heine V and Kelly M 1972 *J. Phys. C: Solid State Phys.* **5** 2845
- Henry C H and Slichter C P 1968 *Physics of Color Centers* ed W Beall Fowler (New York: Academic)
- Jones W B and Thron W J 1980 *Continued Fractions—Analytic Theory and Applications (Encyclopedia of Mathematics and its Applications vol II)* (Reading, MA: Addison Wesley)
- Jurczek E 1985 *Phys. Rev. B* **32** 4208
- Lambin P H and Gaspard J P 1982 *Phys. Rev. B* **26** 4356
- Lanczos C 1950 *J. Res. NBS* **45** 255
- Maradudin A A 1969 *Progress in Physics: Lattice Dynamics* (New York: Benjamin)
- Montroll E W 1942 *J. Chem. Phys.* **10** 218
- Poussigie G and Benoit C 1989 *J. Phys.: Condens. Matter* **1** 9547
- Poussigie G, Benoit C, Sauvajol J-L, Lere-Porte J-P and Chorro C 1991 *J. Phys.: Condens. Matter* **3** 8803
- Quiming Li, Soukoulis C M and Grest G S 1990 *Phys. Rev. B* **41** 11713
- Royer E 1989 *Rap. Stage DEA Modèles Théoriques de la Physique Montpellier*
- Royer E, Benoit C and Poussigie G 1992 *J. Phys.: Condens. Matter* **4** 4561
- Saad Y 1980 *Lin. Alg. Appl.* **34** 269
- 1981 *Math. Comput.* **37** 105
- Scheunders P and Naudts J 1990 *Z. Phys. B* **80** 423
- Shohat J A and Tamarkin J D 1963 *The Problem of Moment (Math. Surveys I)* (Providence, RI: American Mathematical Society)
- Stieltjes T J 1884 *Ann. Ecole Normale* **1** 52
- 1894 *Ann. Fac. Sci. Toulouse (Fr)* **8** J1-122
- Su W P, Schrieffer J R and Heeger A 1980 *Phys. Rev. B* **22** 2099
- Turchi P, Ducastelle F and Treglia G 1982 *J. Phys. C: Solid State Phys.* **15** 2891
- Wall H S 1948 *Analytic Theory of Continued Fractions* (Princeton, NJ: Van Nostrand)
- Wheeler J C, Prais M G and Blumstein C 1974 *Phys. Rev. B* **10** 2429
- Williams M L and Maris H J 1985 *Phys. Rev. B* **31** 4508