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Impurity States and the Transfer Matrix Approach: An Elementary Example*

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The single impurity problem for the classical linear chain is solved exactly using the Transfer Matrix approach to calculate the densities of states of excitations (phonons). This paper is a didactic presentation to illustrate how the formalism works in a simple case, having in mind future extensions to deal with problems on disordered alloys. The same results have been obtained previously by Hori and Asahi (Prog.Theor. Phys. 17, 523 (1957)) and exact calculations for arbitrary dimensions can be found in Maradudin et *al's* paper "Theory of Lattice Dynamics in the Harmonic Approximation" (Solid State Phys Supp. (1963)).

O problema de uma impureza isolada numa cadeia linear clássica é resolvido em forma exata usando o tratamento da Matriz de Transferência para calcular a densidade de estados das excitações (fonons): Este trabalho é uma apresentação didática que deseja ilustrar como o formalismo funciona num caso simples, tendo em mente futuras extensões no estudo de ligas desodernadas. Os mesmos resultados já foram obtidos por Hori e Asahi (Prog.Theor.Phys. *17*, *523* (1957)) e resultados exatos aplicáveis a dimensões arbitrárias se encontram no artigo de Maradudin *et al* "Theoryof Lattice Dynamics in the Harmonic Approximation" (Solid State Phys. Supp. (1963)).

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1. INTRODUCTION

We encounter in theoretical physics a big number of problems which can be solved with the help of the Transfer Matrix (TM) formalism. As a general characteristic, when the method is applicable, the equations of motion of the system show a certain kind of periodicity or regularity (usually in the site representation) in such a way, that we can connect physical properties of equivalent units of the system by successive operation of the so called transference functions (TM). The procedure permits the reduction of the dimensionality of the mathematical problem and the task left consists of calculation of the TM and its corresponding eigenvalues.

Below we shall mention some cases where the method is successfully employed:

a) as a classical example we recall the exact solutions of the one and two-dimensional Ising problem as presented for instance in Mattis' book[1]. In the case of the linear chain a mathematical problem of dimensionality 2^N, with being the total number of spins in the chain, is reduced to find the eigenvalues of a (2x2) TM. The physical properties involved in the transference operation are the site probabilities of having spin up or down. For the surface Ising magnet we also have a reduction of dimensionality (from 2^{N^2} to 2^N) when the TM approach is used. Finally, in both problems, the partition function is calculated using the TM eigenvalues;

b) the Krönig-Penney model[2] for a one-dimensional periodic potential can also be solved with the same procedure[3]. Due to the translational invariance the Schrödinger equation is just solved for a unit cell. The TM is then used to match the wave function from one cell to the next;

c) in studying surface properties the method looks particularly well suited to calculate the Density of States (DOS) of semi-infinite crystals, for both the electronic and phonon spectra. The method is of rapid convergence and has the advantage of being exact once the Hamiltonian of the system is known[4]. The method has become very popular and has been used by a big number of authors[4] to calculate surface DOS.

Our interest in the formalism is concerned with the phonon spectra of disordered alloys, a problem which can be approached with an extension of the TM method[5]. We want to present here, as a first elementary step when moving in that direction, an exact study of the phonon **DOS** for the classical linear chain of harmonic oscillators when a sustitutional impurity is introduced in the system. Due to the simplicity of the problem it will result easy to illustrate the central ideas around the TM approach, and we will sperid some effort in doing that in detail.

Although beirig known that the atomic linear chain does not possess long range order at finite temperature[6], it represents one of the most used examples in Solid State physics and it is quoted in the majority of the classical textbooks in the field[7].

The instability of the linear chain, which is related to a divergent contribution of fluctuations for a one-dimensional system, can be supressed if we assume the presence of another interaction of higher dimensional character (like three-dimensional electronic cohesion). If this interaction is weakly coupled to the atomic oscillations we can still treat the system as one-dimensional (or quasi-one-dimensional) when concerning the phonon properties. In what follows, and without explicit reference to that fact, we will assume that we are dealing with one of such systems.

Firstly we will solve the case of a perfect monoatomic linear chain. This problem is used to define the Green function formalism and to show how the method can be used to calculate the DOS per atom. The TM is employed to solve an infinite set of equations for the different Green functions in the site representation.

The boundary conditions satisfied by the physical solutions of the TM are discussed and their physical meaning is made clear through the use of our explicit example.

Once the relevant quanrities are defined by solving the above mentioned trivial problem, we proceed to break the translational symmetry by introducing a *substitutional* impurity in the chain. It is shown in this work how the TM method can also handle this case even in the absence of translational invariance. The procedure is exactly similar to the approãch used to study electronic surface states. In this latter case the presence of the surface has also broken the translaticna! symnietry in one of the spatial directions[4], nevertheless the TM formalism can be used to solve the problem for the bulk crystal.

Localized states around the impurity are obtained when the impurity mass is smaller than the atomic mass characterizing the perfect chain. This fact can be understood physically, since a light impurity atom will oscillate at frequencies which are unattainable for the more massive atoms of the chain.

2. THE PERFECT MONO-ATOMIC CHAIN AND THE GREEN FUNCTION FORMALISM

Our system, consisting of a collection of N identical harmonic oscillators, is shown in Fig.1. The quantities $\underline{K}$ and $\underline{m}$ are the spring constant and the atomic mass respectively. The deviations of atoms from their equilibrium positions are denoted by $q_\nu(t)\,(\nu = 1,2,\ldots,N)$, and periodic boundary conditions are assumed from the beginning:

$$q_{N+1} \equiv q_1 \tag{1}$$

The well known Lagrangian of the system is given by

$$L = \frac{1}{2}\, m \sum_{\nu} \dot{q}_\nu^2 - \frac{1}{2}\, m\, \omega_0^2 \sum_{\nu} (q_{\nu+1} - q_\nu)^2 , \tag{2}$$

where $\omega_0 = (K/m)^{1/2}$ is the natural frequency of the oscillators. If we look for a harmonic solution $q_\nu(t) = A_\nu\, e^{i\omega t}$ of the equations of motion we get the relations

$$-\omega^2 A_\nu = \omega_0^2 (A_{\nu+1} + A_{\nu-1} - 2A_\nu) , \quad \nu = 1,2,\ldots,N . \tag{3}$$

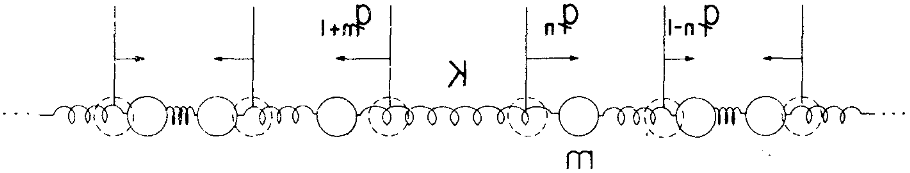

Fig.1 - The monoatomic linear chain showing the atom displacement for an arbitrary configuration.

The former equations can be written in matrix form by using the N-dimensional amplitude vector

$$\underset{\sim}{A} \equiv \begin{bmatrix} A_1 \\ A_2 \\ \\ \\ A_N \end{bmatrix} \tag{4}$$

and $(N\times N)$ matrices for the kinetic and potential energy. The complete set of equations given by (3) reduces to

$$\omega^2\ 1\cdot\underset{\sim}{A} = (T + V)\ \cdot \underset{\sim}{A} \tag{5}$$

where 1 is the $(N\times N)$ identity and the others matrices are defined by

$$\begin{aligned} T_{\nu\sigma} &\equiv 2\omega_0^2\ \delta_{\nu\sigma} \\ V_{\nu\sigma} &\equiv -\ \omega_0^2(\delta_{\nu,\sigma+1} + \delta_{\nu,\sigma-1})\ . \end{aligned} \tag{6}$$

This notation will prove useful in future calculations.

Going back to the set of equations (3) we note that their structure is independent of the index ν (site index). In other words, the matrix elements of T and V, in the representation used, are independent of the site index.

This is one of the conditions which allows us to use the TM to hop from ona site to the next. If we define a transfer function (TM) by

$$\phi(\omega)A_\nu \equiv A_{\nu+1}\ , \tag{7}$$

insertion of this definitions into the systeni (3) yields the following equation for $\phi(\omega)$

$$\omega_0^2\phi^2 + (\omega^2 - 2\omega_0^2)\phi + \omega_0^2 = 0\ . \tag{8}$$

Eq.(8), being a second degree algebraical equation, has two solutions given by

$$\Phi_{\pm}(\omega) = 1 - \frac{1}{2}(\omega/\omega_0)^2 \pm \frac{1}{2}(\omega/\omega_0)^2 \left[1 - 4(\omega_0/\omega)^2\right]^{1/2} \tag{9}$$

One of the conditions to be satisfied by the physical solution is

$$\lim_{|\omega|\to\infty} \Phi(\omega) = 0 \ , \tag{10}$$

meaning that the system will *not* be *able to respond* to perturbations of very high frequencies.

Concerning propagation along the chain we can distinguish two regimes:

a) for $\omega^2 > 4\omega_0^2$ the TM is real and the solution satisfying the condition (10) is

$$\Phi(\omega) = 1 - \frac{1}{2}(\omega/\omega_0)^2 + \frac{1}{2}(\omega/\omega_0)^2 \left[1 - 4(\omega_0/\omega)^2\right]^{1/2}$$

which can be rewritten in exponential form

$$\Phi(\omega) = -e^{-\beta(\omega)} \ , \tag{11}$$

where

$$\beta(\omega) \equiv \tanh^{-1}\left\{ \frac{(\omega/\omega_0)^2\left[1-4(\omega_0/\omega)^2\right]^{1/2}}{(\omega/\omega_0)^2 - 2} \right\} > 0 \ . \tag{12}$$

The physical picture corresponding to this case is that a perturbation with a frequency $|\omega|>2\omega_0$ induced at an arbitrary site will be damped by a factor $(-)e^{-\beta}$ when going to the next atom. The net result is *no propagation along the chain;*

b) for $\omega^2<4\omega_0^2$ the TM is complex and can be written as an unitary complex number

$$\Phi_{\pm}(\omega) = e^{\pm i\alpha(\omega)} \ , \tag{13}$$

where the phase $\alpha(\omega)$ is given by

$$\alpha(\omega) = \cos^{-1}\left[1 - \frac{1}{2}(\omega/\omega_0)^2\right] . \tag{14}$$

As a result we note that an oscillation with a frequency ω in this range, will propagate from one site to the next by just changing its phase in $\pm\alpha(\omega)$. The TM sign in (13) has to be chosen so as to yield a *positive density of states* after criteria that we will show soon in this section.

As a summary we remark that we ger propagation only for frequencies $|\omega| \leqslant 2\omega_0$ and oscillations for $|\omega| > 20$, will be damped in the medium. The cut off frequency $\omega = 2\omega_0$ is associated with the Bragg difraction, which is a typical phenomenum in a periodic structure.

In order to calculate the spsctrum of excitations in our system we define the Green function or resolvent by

$$G(\omega^2) \equiv \left[\omega^2\cdot 1 - T - V\right]^{-1} . \tag{15}$$

The total DOS $\mathcal{D}(\omega^2)$ can *be* calculated from the resolvent by

$$\begin{aligned}\mathcal{D}(\omega^2) &\equiv -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,G(\omega^2+i\varepsilon)\big|_{\varepsilon\to 0^+}\\ &= -\frac{1}{\pi}\,\mathrm{Im}\lim_{\varepsilon\to 0^+}\sum_{\nu} G_{\nu\nu}(\omega^2+i\varepsilon) ,\end{aligned} \tag{16}$$

where Im means imaginary part and Tr means the trace over the site representation.

it is well known that the eigenvalues of our problem are real and positive[8]. Writing as $\Omega_3^2 > 0$ the eigenvalues of $(T+V)$ and using a representation where G is diagonal we get

$$\begin{aligned}\mathcal{D}(\omega^2) &= -\frac{1}{\pi}\,\mathrm{Im}\lim_{\varepsilon\to 0^+}\sum_{j}\frac{1}{\omega^2 - \Omega_j^2 + i\varepsilon}\\ &= \sum_{j}\delta(\omega^2 - \Omega_j^2) ,\end{aligned} \tag{17}$$

and integration over the energy yields the total number of states

$$\int_0^{m} d\omega^2 \; \mathcal{D}(\omega^2) = N \; . \qquad (18)$$

It is also possible to define a spectral DOS per site taking the diagonal elements of the resolvent

$$\mathcal{D}_\nu(\omega^2) \equiv - \frac{1}{} \; \mathrm{Im}\; G_{\nu\nu}(\omega^2 + i\varepsilon) \; . \qquad (19)$$

In this case the normalization condition is

$$\int_0^{\infty} d\omega^2 \; \mathcal{D}_\nu(\omega^2) = 1 \; . \qquad (20)$$

From the definition of the resolvent operator we obtain what is known as the Dyson equation

$$\omega^2 \; G(\omega^2) = (T+V) \cdot G + 1 , \qquad (21)$$

which yields, by taking matrix elements, the following set of relations

$$(\omega^2 - 2\omega_0^2) \; G_{\nu\mu} = \delta_{\nu\mu} - \omega_0^2 (G_{\nu-1,\mu} + G_{\nu+1,\mu}) \qquad (22)$$

Again, as in the case of the amplitudes, the structure of the equations does nat depend on the site indices. This fact allows us the use of transfer functions (TM) for solving the system of equations given by (22). Defining these functions by

$$\chi \cdot G_{\nu\mu} \equiv G_{\nu+1,\mu} \qquad (23a)$$

for $\nu \geqslant \mu$, and

$$\psi \cdot G_{\nu\mu} \equiv G_{\nu-1,\mu} \qquad (23b)$$

for $\nu \geqslant \mu$, we note that separate substitutions of these relations into equation (22) conduce to equation (8), both for χ and ψ. Incidentally we remark that χ and ψ do not represent inverse operations of each other since they act on different subspaces. Moreover, due to the fact that propagation to the right and to the left are equivalent in a monoatomic linear chain with periodic boundary conditions, the only possibility left is given by

$$\chi = \psi = \phi \; . \tag{23}$$

Using now the relations $G_{\nu+1,\mu} = \phi G_{\nu\nu}$ and $G_{\nu-1,\mu} = \phi G_{\nu\nu}$ we obtain

$$G_{\nu\nu}(\omega^2) = \left[(\omega^2 - 2\omega_c^2) + 2\omega_0^2\, \phi(\omega^2)\right]^{-1} \tag{24}$$

As before, two cases must be considered:

a) for $\omega^2 > 4\omega_0^2$, that is when no propagation is present, the TM $\phi(\omega^2)$ is real yielding a vanishing DOS. Excitations of the system are restriated to the band $0\ 6\ \omega^2 \leqslant 4\omega_0^2$. The sign of ϕ_+ outside the band is determined by the condition (10);

b) inside the band the TM is an unitary complex number and therefore there is a net contribution to the DOS. The correct sign of ϕ_+ is now determined through the use of relations (24) and (19), *so* as to *yield* a *positive* DOS. In this case the proper TM is given by $\phi_+(\omega^2)$ and the site density of states results in

$$\mathcal{D}_\nu(\omega^2) = \begin{cases} 0 \quad \text{for } \omega^2 > 4\omega_0^2 \;, \\[2ex] \dfrac{1}{\pi\sqrt{\omega^2(4\omega_0^2 - \omega^2)}} \quad \text{for } 0 \leqslant \omega^2 \leqslant 4\omega_0^2 \; . \end{cases} \tag{25}$$

The graph of $\mathcal{D}_\nu(\omega^2)$ is shown in Fig. 2. It displays the typical DOS for a one-dimensional system with Van Hove's singularities of the inverse square-root-type. Since $\mathcal{D}_\nu(\omega^2)$ is independent of the site index — for this specific example worked out here —, the total DOS $\mathcal{D}(\omega^2)$ is just given by

$$\mathcal{D}(\omega^2) = N\mathcal{D}_\nu(\omega^2) \; ,$$

where N is the total number of oscillators.

Up to now our example is trivial and all we have done is to rederive well known results with a rather sophisticated formalism (like

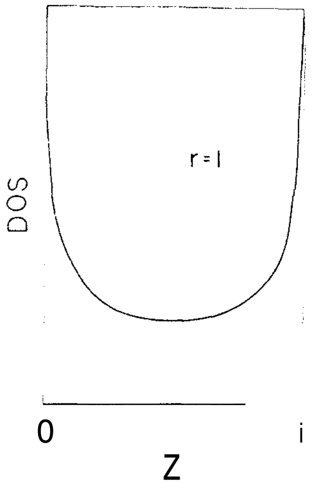

Fig.2 - The single site DOS for the perfect monoatomic chain. The area under the graph is normalized to 1, since this is the total number of degrees of freedom per site. The variable z used for the abscissa is defined as $z \equiv \omega^2/4\omega_0^2$, meaning that a value of $z = 1$ corresponds to the cut-off frequency $\omega_c = 2\omega_0$.

"cracking a nut with a hydraulic hammer"). In the next section we will solve the same problem when putting an impurity in the chain, and the formalism already developed will prove economic and elegant.

3. IMPURITY STATES: LOCALIZED MODES

Assuming that a substitutional impurity of mass $M \neq m$ is located at the site ν_0, as shown by Fig.3, the equations of motion now yields

$$\omega^2 A_\nu = \omega_0^2 (2A_\nu - A_{\nu+1} - A_{\nu-1}), \ \nu \neq \nu_0 \ , \tag{26}$$

and

$$\omega^2 A_{\nu_0} = r\omega_0^2 (2A_{\nu_0} - A_{\nu_0+1} - A_{\nu_0-1}) \ , \tag{27}$$

where the factor r is the ratio between the masses entering in our problem, i.e.

$$r \equiv \frac{m}{M} \ . \tag{28}$$

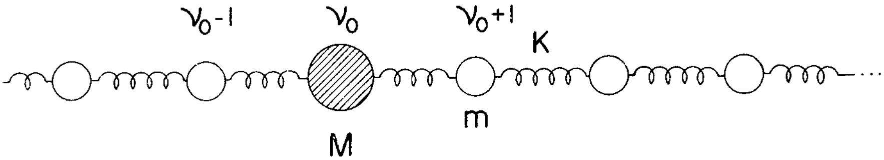

Fig.3 - The linear chain with a impurity atom. In the case considered we are assuming that the spring constants are not changed and the impurity is only characterized by a different mass.

The matrix eiements for the kinetic and potential energy are now given by

$$T_{\nu\mu} = 2\omega_0^2\, \delta_{\nu\mu}\left[1 + (r-1)\delta_{\nu\nu_0}\right] ,$$
$$V_{\nu\mu} = -\,\omega_0^2(\delta_{\nu,\mu+1}+\delta_{\nu,\mu-1})\left[1+(r-1)\delta_{\nu\nu_0}\right] . \tag{29}$$

Due to the presence of the impurity the site DOS will not be independent of the site index now. The interesting quantity to calculate is $\mathcal{D}_{\nu_0}(\omega^2)$. The equations for the corresponding Green functions are

$$(\omega^2-2r\omega_0^2)G_{\nu_0\nu_0} = 1 - r\omega_0^2(G_{\nu_0+1,\nu_0} + G_{\nu_0-1,\nu_0}) , \tag{30a}$$

$$(\omega^2-2\,\omega_0^2\,)G_{\nu\nu} = 1 - \omega_0^2(G_{\nu+1,\nu} + G_{\nu-1,\nu}) , \tag{30b}$$

if $\nu \neq \nu_0$, and

$$(\omega^2-2\omega_0^2)G_{\nu_0\pm\sigma,\nu_0} = -\,\omega_0^2(G_{\nu_0\pm\sigma+1,\nu_0} + G_{\nu_0\pm\sigma-1,\nu_0}) \tag{30c}$$

for $\sigma = 1,2,3,\ldots$.

Although the translation symmetry is broken, tne equations of motion still have a regular pattern when hopping to the right or to the left of the impurity site. The TM approach still works in this case if the restriction of *never crossing the impurity* site is fulfilled. Again due to symmetry we must have

$$G_{\nu_0+1,\nu_0} = \phi G_{\nu_0\,\nu_0},$$

and

$$G_{\nu_0-1;\nu_0} = \phi G_{\nu_0 . \nu_0}$$

Inserting the latter relations in equation (30a) yields

$$G_{\nu_0,\nu_0}(\omega^2,r) = \left[(\omega^2-2r\omega_0^2) + 2\phi(\omega^2)r\omega_0^2\right]^{-1} , \qquad (31)$$

where the sign of the TM has to be chosen in the same way as in the case of the perfect lattice. If we do that choice properly we find two cases:

I. For $0<r\leqslant 1$ no localized states are present. The corresponding DOS is given by

$$\mathcal{D}(\omega^2) = \frac{r}{\pi} \cdot \frac{\sqrt{(4\omega_0^2 - \omega^2)\omega^2}}{\omega^2\left[4r^2\omega_0^2-(2r-1)\omega^2\right]} , \quad 0 < r \leqslant 1 , \qquad (32)$$

and two examples are shown in Fig.4. Note that for small r (big impurity case) there is a marked depletion of states in the neighborhood of the upper band edge. This fact is physically understandable since oscillations

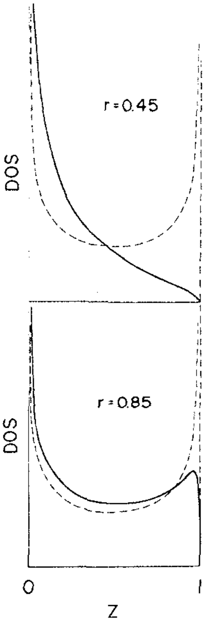

Fig.4 - The DOS at the impurity site for values of $r < 1$. The pure monoatomic case is also shown in dashed line for comparison. We note a shift of states to the low frequency side of the spectrum, which is consistent wirh the fact that the impurity is more massive than the rest of the atom*.

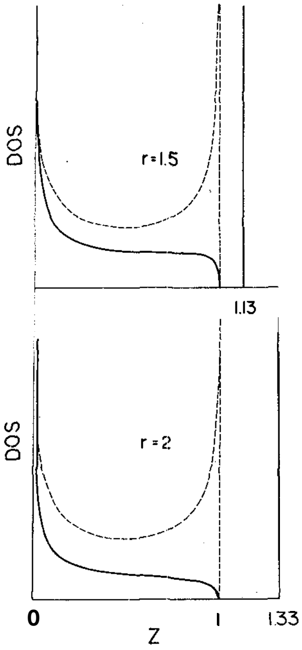

Fig.5 - The DOS at the impurity site for light impurity masses. Again the DOS for the perfect linear chain is shown for comparison purposes. Note that the area under the graph, which represents the fractional number of non localized states, *is visible smaller than* in the perfect case. The fractional number of states lacking is associated to the δ-function localized state splitted off from the continuum. The variable z used in the graph is defined under Fig.2.

of more massive atoms should shift to lower frequencies. The character of the Van Hove's singularity at the upper band edge has also changed to the square root type. For r close to one a peak is developed in the DOS in a kind of a resonant state.

No localized states are present since a massive impurity will force the chain to oscillate following its lower frequency motion.

II. For $r > 1$ we got states outside the band $0 < w^2 < 4\omega_0^2$. *Those states are of localized character* since for energies in that range *the* TM *is exponentially decaying* as indicated by relation (11). Two examples are shown in Fig. 5 displaying δ-function localized states splitted off in the high frequency region. The physical picture in this case is a light impurity oscillating at high frequencies, whose oscillations can not be followed by the sorrouding more massive atoms.

The density of states at the impurity site can be written in closed form. The result is

$$\mathcal{D}_{\nu_0}(\omega^2) = \begin{cases} \dfrac{r}{\pi} \dfrac{\sqrt{(4\omega_0^2-\omega^2)\omega^2}}{\omega^2\left[4r^2\omega_0^2-(2r-1)\omega^2\right]} , & \text{for } \omega^2 \leqslant 4\omega_0^2 , \\ \\ \dfrac{2(r-1)}{2r-1} \cdot \delta(\omega^2 - \dfrac{4r^2}{2r-1}\omega_0^2) , & \text{for } \omega^2 > 4\omega_0^2 . \end{cases}$$

Both aensities of states given by relations (32) and (33) are properly normalized to one.

In the next section we do the final remarks and discussions.

4. FINAL DISCUSSIONS

Here we have solved the problem of the phonon spectrum in the case of a single impurity in a monoatomic linear chain. This work is part of a wider prograni aimed to study the properties of disordered alloys and disordered magnetic materials with particular interest in the calculation of the excitation spectra *of* those systems.

We have illustrated here the use of the TM formalism to deal with a problem of this kind. The method can be extended and combined with several approximation schemes to treat disordered systems[5,9]. Sometimes exact solutions can be obtained as in the example shown in this paper.

In closing this section and concerning to our results, we want to remark the following:

i) when the impurity mass is smaller than the massof the atoms forming the chain, we get localized states splitted off from thecontinuum for the DOS at the impurity site;

ii) for the small irnpurity concentration regime (dilute alloy), when no correlations between impurities is expected, a simple superposition of isolated impurity problems should describe fairly well the behavior of the system;

iii) as long as the concentration of impurities increases a larger number of states is removed from the band and finally this set of δ-function singularities generates an impurity band for the total DOS. Usually a rounding of the sharp DOS edges corresponding to the pure case is also obtained for the disordered alloy, and a change in character of Van Hove's singularities should also be expected. Work is under progress to study those problems.

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