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Finite chains

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Wave propagation in finite media (and, in general, the motion of continous, finite media) is a standard subject of differential equations with boundary conditions. In solids it acquires some particularities, arising from the discrete (atomistic) nature of solids, from their periodicity and, possibly, from surface (edge) modifications. The later point is particularly emphasized in solids in relation to the surface (Tamm or Shockley) electronic states.[1]-[3] Less known are the modification of the periodic positions of atoms near the surface, due to anharmonic forces.[4]

A convenient simplification of the problem is obviously its reduction to a one-dimensional chain. First, we consider here a semi-infinite chain extending from $n = 0, 1, ...$to $n \to \infty$. The typical problem is provided by the tight binding approximation to the electron motion, described by the equations

$$\varepsilon a_n = t(a_{n+1} + a_{n-1}) \ , \ n = 1, 2, ... \ ,$$
$$\varepsilon a_0 = t a_1 \ ; \tag{1}$$

here ε is the on-site energy, a_n are the annihilation operators of the electron states (amplitudes of the atomic orbitals in the tight-binding waefunction) and t is the transfer amplitude between two neighbouring sites (hoping matrix element of the electronic hamiltonian between two adjacent atomic orbitals); we assume $t > 0$ (and ε real). Equations (1) are the equations of motion for a_n with the hamiltonian $\sum_{<nn'>} t a_n^+ a_{n'}$, where the summation extends over the nearest-neighbours. We note the absence of an original on-site reference energy ($\varepsilon = 0$ for $t = 0$) and the same parameters (on-site energy and t) for the chain edge $n = 0$. Such types of finite-difference equations have been studied extensively for various types of waves, like elastic waves, spin waves, etc.[5]-[8]

The solutions of equations (1) are of the form $a_n \sim r^n$; introducing them in the regular set of equations (1) we get $r^2 - 2\lambda r + 1 = 0$, *i.e.* $r_{1,2} = \lambda \pm \sqrt{\lambda^2 - 1}$, where $2\lambda = \varepsilon/t$. For $|\lambda| \leq 1$ we may choose $\lambda = \cos k$, $r_{1,2} = e^{\pm ik}$ and the general solution $a_n = Ae^{ikn} + Be^{-ikn}$. We note that the solution is periodic with period $\Delta k = 2\pi$, so we may limit ourselves to $-\pi < k \leq \pi$ (the first Brillouin zone). The edge equation (1) gives $2\cos k(A + B) = Ae^{ik} + Be^{-ik}$, or $Ae^{-ik} + Be^{ik} = 0$ (which formally is $a_{-1} = 0$), *i.e.* $A \sim e^{ik}$, $B \sim -e^{-ik}$. It follows that the solution reads $a_n = c(k)\sin(n + 1)k$, with the property $c(-k) = -c(k)$, *i.e.* we should limit ourselves to half the Brillouin zone $0 < k < \pi$ (as for standing waves) and write the general solution as

$$a_n = \int_{-\pi}^{\pi} dk c(k)\sin(n + 1)k = 2\int_0^{\pi} dk c(k)\sin(n + 1)k \ , \ c(k) = \frac{1}{\pi}\sum_{n=0} a_n \sin(n + 1)k \tag{2}$$

and $\varepsilon(k) = 2t\cos k$, *i.e.* a sin-Fourier series. We note also that $\sin(n + 1)k/\sin k$ as a polynomial of $\cos k = \lambda$ is the Gegenbauer polynomial of the first order.[5] Therefore, the semi-infinite chain

of tight-binding electrons exhibit the energy band of the infinite chain, the effect of the edge being only to reflect the motion (and produce standing waves which diminish the Brillouin zone to half). For $|\lambda| > 1$, we may choose $\lambda = \cosh k$, $r_{1,2} = e^{\pm k}$ and $a_n = Ae^{-kn}$ for $k > 0$ ($a_n = Ae^{kn}$ for $k < 0$); it is easy to see that the edge equation (1) is not satisfied. Actually, this equation has modified parameters (*i.e.* $a_{-1} \neq 0$); for instance, if it is writen as $(2\lambda - \alpha)a_0 = a_1$, then we have the damped solution $a_n = Ae^{-kn}$ for one value of k given by $e^k = \alpha$ (> 1); this is a (Tamm) surface (edge) state.

We consider now a finite chain with $N + 1$ sites, described by the equations

$$\begin{aligned} \varepsilon a_N &= t a_{N-1} \ , \\ \varepsilon a_n &= t(a_{n+1} + a_{n-1}) \ , \ n = 1, 2, ...N - 1 \ , \\ \varepsilon a_0 &= t a_1 \ ; \end{aligned} \tag{3}$$

we proceed in the same manner, and get $\lambda = \cos k$ for $|\lambda| \leq 1$, $a_n = Ae^{ikn} + Be^{-ikn}$, restricted to the first Brillouin zone $-\pi < k \leq \pi$; the two boundary conditions give

$$\begin{aligned} Ae^{ik(N+1)} + Be^{-ik(N+1)} &= 0 \ , \\ Ae^{-ik} + Be^{ik} &= 0 \ , \end{aligned} \tag{4}$$

i.e. $\sin(N + 2)k = 0$, $k = \frac{\pi}{N+2}m$, $-(N + 1) \leq m \leq N + 2$ and $a_n \sim e^{ik(n+1)} - e^{-ik(n+1)}$, *i.e.* standing waves again; we limit ourselves to half the Brillouin zone and the solution is given by the same equation (2)

$$\begin{aligned} a_n &= \tfrac{\pi}{N+2} \textstyle\sum_{-\pi<k\leq\pi} c(k) \sin(n + 1)k = \tfrac{2\pi}{N+2} \textstyle\sum_{0\leq k\leq\pi} c(k) \sin(n + 1)k \ , \\ c(k) &= \tfrac{1}{\pi} \textstyle\sum_{n=0}^{N} a_n \sin(n + 1)k \end{aligned} \tag{5}$$

with the diference that the energy is $\varepsilon_m = 2t \cos[\pi m/(N + 2)]$; actually, we should leave aside the values $k = 0$ and $k = \pi$ (likewise for the semi-infinite chain), since $a_n = 0$ for these values; it is easy to see that we have $N + 1$ states. However, for the orthogonality of the Fourier transforms in equation (5) it is necessary to perform the summation over m from $-(N + 2)$ to $(N + 2)$.

The chain described by equations (3) can be viewed as the chain with fixed ends ($a_{-1} = a_{N+1} = 0$); a chain with free ends would imply the vanishing of the derivatives of a_0, a_N. We may also impose the cyclic condition, *i.e.* we require $a_0 = a_{N+1}$ (and $a_{-1} = a_N$) and write the equations of motion as

$$\begin{aligned} \varepsilon a_N &= t(a_{N-1} + a_0) \ , \\ \varepsilon a_n &= t(a_{n+1} + a_{n-1}) \ , \ n = 1, 2, ...N - 1 \ , \\ \varepsilon a_0 &= t(a_1 + a_N) \ ; \end{aligned} \tag{6}$$

we get $k = \frac{2\pi}{N+1}m$ and traveling waves $a_n = c(k)e^{ikn}$. We can see that the position of the eigenvalues does not depend relevantly on the boundary conditions for large N (in the thermodynamic limit; compare $k = \frac{2\pi}{N+1}m$ for cyclic condition and $k = \frac{\pi}{N+2}m$ for fixed ends). This is known as the Ledermann theorem (for short-range forces).[9, 10] However, their density can change; *e.g.*, the eigenvalues are twice as rare for cyclic condition than for fixed ends; fixed ends or free ends are practically cyclic condition for a chain with a double length.[7] The number of states is the same

in the thermodynamic limit, since for fixed or free ends, where the eigenvalues are denser, we sum only over half the Brillouin zone.

The case $|\lambda| > 1$, $\lambda = \cosh k$ for the finite chain has a solution only if we modify the edge parameters.

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