Local vibrational mode of an impurity in a monatomic linear chain under open and periodic boundary conditions

Qiang Luo

Department of Physics, Renmin University of China, Beijing, 100872, People’s Republic of China

E-mail: qiangluo@ruc.edu.cn

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Abstract

In this paper, we revisit the lattice vibration of a one-dimensional monatomic linear chain under open and periodic boundary conditions, and give the exact conditions for the emergence of the local vibration mode when one of the atoms is replaced by an impurity. Our motivation is twofold. Firstly, in deriving the dispersion relation of the atoms, the periodic boundary condition is overwhelmingly utilized while the open boundary condition is seldom used. Therefore we manage to obtain the dispersion relation under both boundary conditions simultaneously by the Molinari formula. Secondly, in the presence of an impurity, the local vibration mode can emerge as long as the mass of the impurity $m'$ is smaller than the mass of the perfect atom $m$ to a certain degree, which can be measured by the mass ratio $\delta = \frac{m - m'}{m}$. At the periodic boundary condition, the critical mass ratio is 0 or $\frac{1}{N}$, depending on whether the length $N$ of the chain is even or odd. At the open boundary condition, the critical mass ratio is $\frac{N}{(2N + 1)(2N + 3)}$ if the impurity locates at the end of the chain, while it is $\frac{N}{(2N + 1)(2N + 3)}$ with $N_l$ and $N_r$ the number of atoms at the left- and right-hand sides of the impurity if the impurity locates at the middle.

Keywords: monatomic linear chain, boundary condition, local vibrational mode, Molinari formula

(Some figures may appear in colour only in the online journal)
1. Introduction

The physical properties of low dimensional materials have attracted the attention of physicists, particularly in the context of the synthesis of carbon nanotubes and graphene [1], therefore we are interested in revisiting the enduring topic of lattice vibration of one-dimensional (1D) linear chains. In the perfect crystal lattice, the atoms vibrate along their own equilibrium positions incessantly, and the interaction among them makes those local vibrations connect, which, of course, produces the so-called lattice wave. Impurities, however, are known to affect the vibrational properties of crystals by modifying the distribution of normal modes and thus may induce some unusual vibrational modes [2].

The 1D monatomic linear chain and diatomic linear chain are workhorses for the illustration of lattice waves as well as acoustic and optical branches. In the case of nearest neighbor interactions and harmonic approximation, the equation of motion of each individual atom is governed by the Newton’s second law. For the finite chain we must specify how the atoms at the two endpoints are to be described to avoid possible ambiguity. It is generally believed that the boundary condition is not of significant importance in the infinite chain since it fails to alter the final results essentially. The standard textbooks on solid state physics [3–5], without exception, will tell us to avoid the cumbersome open boundary condition (OBC) and instead utilize the periodic boundary condition (PBC), based on which only one or two algebraic equations are needed to obtain the dispersion relation of monatomic or diatomic chains. Although in most cases the bulk properties of infinite chains do not rely on the boundary condition, it does make a difference if the length of chain is finite. Furthermore, the PBC prevents us from studying surface effects. The overwhelming utilization of the PBC in the derivation of the dispersion relations in most available materials will certainly mislead students, who may underestimate the true effect of the boundary condition.

Historically, the vibration frequencies of 1D lattices with PBC and OBC were studied by Max Born in a series of papers, although the solution to the OBC case is not really exact. Later Halford [6] and Wallis [7] rederived the dispersion relation with the OBC with the help of the determinants of two special cases summarized by Rutherford [8, 9]. To explain the differences between the PBC and OBC, we shall take the local vibration due to the impurity as an example. It is expected that the boundary condition will alter the condition for the emergence of the local vibration.

For simplicity we concentrate on the 1D monatomic linear chain, while the 1D diatomic linear chain is left for the motivated reader. Our paper is organized as follows. In section 2 we introduce the Molinari formula, through which we derive the dispersion relation of the 1D monatomic chain under open and periodic boundary conditions. In section 3 we give the exact conditions for the emergence of the local vibration mode of the impurity at different positions of the linear chain and at different boundary conditions. The local vibration frequency and amplitude are presented in section 4. Section 5 is devoted to our conclusions.

2. The dispersion relation of a 1D monatomic chain

We shall review the dispersion relation of a 1D monatomic chain where only one atom per primitive cell of lattice constant $a$ and force constant $\beta$, formed by $N$ atoms of mass $m$. The $n$th atom oscillates around its equilibrium position $na$ with the displacement $u_n$. With the simple harmonic approximation and the nearest neighbor approximation the motion of the $n$th atom can be given by Newton’s law
\[
m\frac{d^2u_n}{dt^2} = -\beta(-u_{n-1} + 2u_n - u_{n+1})
\]  
(1)

with \( n = 1, 2, \ldots, N \). The PBC—which means that when we come to the end of the atomic chain we assume that the chain identically repeats itself—is used, i.e. \( u_0 = u_N \) and \( u_{N+1} = u_1 \). In the OBC, however, the equations of motion of the two atoms sitting at the boundary are

\[
\begin{align*}
\frac{d^2u_1}{dt^2} &= -\beta(u_1 - u_2) \\
\frac{d^2u_N}{dt^2} &= -\beta(-u_{N-1} + u_N)
\end{align*}
\]  
(2)

The set of discrete coupled differential equations can be solved by means of travelling waves with wavevector \( q \) and frequency \( \omega \), of the form

\[
u_n(t) = \tilde{u}_q(n)e^{-i\omega t}.
\]  
(3)

Using the equations above we therefore arrive at the secular equation of the monatomic chain

\[
M^{(l)}\tilde{U} = 0
\]  
(4)

where \( \tilde{U} = (\tilde{u}_q(1), \tilde{u}_q(2), \ldots, \tilde{u}_q(N))^T \), and

\[
M^{(l)} = \begin{pmatrix}
1 + l - E & -1 & & & \\
-1 & 2 - E & -1 & & \\
& \ddots & \ddots & \ddots & \\
& & -1 & 2 - E & -1 \\
& & & -1 & 1 + l - E
\end{pmatrix}
\]  
(5)

with \( E = m\omega^2/\beta \), and \( l = 0 \) and \( 1 \) for the OBC and PBC, respectively. The non-trivial solution to (4) exists unless the determinant of the coefficient matrix (5) equals zero, i.e. \( |M^{(l)}| = 0 \). The determinant of (5), a tridiagonal matrix, can be calculated by various methods, such as the Chebyshev polynomial method (see appendix A) and the Molinari formula method (see appendix B).

The tridiagonal matrix and its generalized form, which are of analytical and numerical importance, have had an extensive and profound influence on physics due to their unique mathematical structures. On the one hand, the tight-binding approximation and the nearest neighbor interaction approximation allow us to transform the Hamiltonians of numerous ideal models to tridiagonal matrices. On the other hand, it is possible to reduce the Hamiltonian of any physical problem to a tridiagonal matrix by virtue of some standard numerical algorithms such as the Lanczos method. We shall mention here that a determinant should be in hand to obtain the quantum fluctuation factor of the harmonic oscillator in the framework of Feynman’s path integral [10].

Abundant methods have been discovered in view of the widespread applications of the determinant of these tridiagonal matrices. Rutherfold [8, 9] had already summarized many useful conclusions relating to the determinant that had made their appearances in physics and chemistry around the middle of the last century. The simple and explicit analytic expression which is used to calculate the determinant of arbitrary tridiagonal matrices, however, is absent until about two decades ago when Molinari finally found such a splendid formula [11, 12]. The Molinari formula is powerful in that it can handle the tridiagonal matrices whose diagonal elements and/or offdiagonal elements are not necessarily the same. This feature makes it possible for us to settle the impurity problem, which will come in subsequent sections. From the Molinari formula we find that
\[
\begin{align*}
|M^{(1)}| &= 2(\cos N\tau - 1) \\
|M^{(0)}| &= -2 \tan \frac{\tau}{2} \sin N\tau
\end{align*}
\]

(6)

where the dimensionless parameter \(\tau \equiv qa\) satisfies \(2 - E = 2 \cos \tau\). The dispersion, therefore, should be

\[E^{(l)} = 2(1 - \cos qa).\]

(7)

Since the dispersion relation is at hand, we can turn to the possible wavevectors which lie in the first Brillouin zone (FBZ), i.e. the Wigner–Seitz unit cell of the reciprocal lattice. In the FBZ, the number of possible vibration wavevectors equals that of the number of degrees of freedom. Besides, the determinant of \(M^{(l)} (l = 0, 1)\) in (6) will be zero on condition that \(\cos N\tau = 1 (l = 1)\) or \(\sin N\tau = 0 (l = 0)\), which fulfills the traditional analysis that \(e^{iNqa} = 1\). For the PBC \((l = 1)\), the wavevectors satisfy the relation \(Nq_l a = 2\pi h_l\), while for the OBC \((l = 0)\) it is \(Nq_0 a = \pi h_0\) where both \(h_l\) and \(h_0\) are some integers. Therefore, the wavevectors in the FBZ should be

\[q_l = \begin{cases} 
2\pi/h_l, & \text{PBC} \\
\pi/N a, & \text{OBC}
\end{cases}
\]

(8)

with \(h_l = -N/2 + 1, -N/2 + 2, \cdots, N/2\) and \(h_0 = 0, 1, \cdots, N - 1\), a set that totally has \(N\) different values [13], and the dispersion relation is shown in figure 1 (see footnote 1).

\footnote{Strictly speaking, the so-called Brillouin zone is illegal for the OBC case in that the translation invariance property does not exist. So, the notation \(q_0\) here should not be regarded as the wavevector, but rather an index for the energy spectrum.}
We now turn to the situation where one of the atoms in the chain is replaced by an impurity with mass \( m' \). It is generally believed that the mass and the position of the impurity will influence the local vibration, the vibration frequency and amplitude for instance. We define the mass ratio

\[
\delta = \frac{m - m'}{m}
\]  

(9)

as the measurement of the relative mass of impurity. Since it is known that the localized vibrational exists only for the light mass impurity \([14]\), in subsequent sections we will discuss the case \( 0 < \delta < 1 \) only under the PBC and OBC, respectively. Further, the maximum vibration frequency (or energy) of the atomic chain with impurities will be larger than that of the corresponding ideal atomic chain at a certain value \( \delta_c \). The value, definitely, is called the critical mass ratio throughout the paper.

3.1. PBC

If the chain is PBC, only the mass of the impurity matters, and the typical matrix similar to (5) is

\[\text{Figure 2.} \text{ The maximal vibration energy } E_{\text{max}}(\delta) \text{ (with } E_0 = 4) \text{ varies with the mass ratios } \delta \text{ for even (blue) and odd (red) number of total atoms. It can be distinguished that for } N = 200/201, \text{ the critical mass for the even case is zero, while for the odd case it satisfies the inequality } 4.95 \times 10^{-3} < \delta_c < 5.00 \times 10^{-3} \text{ (see the inset), in good accordance with the theoretical value } 4.975 \times 10^{-3}.\]
We use the Molinari formula to calculate the determinant, where the properties of the trace are also considered. After some basic algebraic operators we arrive at

$$|M^{(1)}| = 2(\cos N\tau - 1) + 2\delta \tan \frac{\tau}{2} \sin N\tau.$$  

(11)

In the spectra of the atoms, only one of them at most will be the local vibration energy, depending on the value of the mass ratio \(\delta\). From (7) we know that in the FBZ where \(-\pi < \tau \leq \pi\), if \(\tau\) is larger we can get the higher energy, and thus approach to the local vibration energy. It can be inferred that in the neighborhood of \(\pi\) we should get the critical factor of mass ratio \(\delta_c\). Let \(\tau = \pi + \varepsilon\) where \(\varepsilon\) is a negative but infinitesimal number, we have

$$\cos N(\pi + \varepsilon) - 1 + \delta_c(1 - \cos(\pi + \varepsilon)) \frac{\sin N(\pi + \varepsilon)}{\sin(\pi + \varepsilon)} = 0,$$  

(12)

and from which we get

$$\delta_c = \frac{(-1)^{N+1} + 1}{2N} = \begin{cases} 0, & N = 2, 4, \ldots \\ \frac{1}{N}, & N = 1, 3, \ldots. \end{cases}$$  

(13)

It came as a surprise that the critical mass ratio should show an odd–even effect, which can also be verified numerically as illustrated in figure 2.

In summary, in the PBC case, if the number of the atoms in the chain is even, the condition for the emergence of the local vibration is \(m' < m\), compared to \(m' < m(1 - 1/N)\) for the odd case. However, in the limit where \(N \to \infty\), the odd–even effect vanishes and the critical mass ratios are the same for the two cases as the bulk behaviors.

3.2. OBC

If the chain is OBC, we should specify the position of the impurity. If the impurity locates at the end of the chain (referred as case \(a\)), say the first entry of the chain, the matrix is

$$M_u^{(0)} = \begin{bmatrix} 1 - (1 - \delta)E & -1 & \cdots & \cdots & \cdots & -1 \\ -1 & 2 - E & -1 & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ -1 & 2 - E & -1 & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ -1 & 2 - E & -1 & \cdots & \cdots & \cdots \end{bmatrix}.$$  

(14)

The determinant of (14) turns out to be

$$|M_u^{(0)}| = -2\tan \frac{\tau}{2} \sin N\tau - 2\delta \cos \left(\frac{N\tau - \tau}{2}\right) \sin \frac{\tau}{2}.$$  

(15)
with the help of the Molinari formula, and the critical mass ratio
\[ \delta_c = \frac{N}{2N-1} \geq \frac{1}{2} \]  
(16)
can be obtained by the same method.

If the impurity locates at the middle of the chain (referred as case \( b \)), where the number of atoms at the left- and right-hand sides of the impurity are \( N_l \) and \( N_r \), respectively. The matrix is
\[
M^{(b)}_b = \begin{pmatrix}
1 - E & -1 & \cdot & \cdot & \cdot \\
-1 & 2 - E & -1 & \cdot & \cdot \\
\cdot & \cdot & \ddots & \cdot & \cdot \\
\cdot & \cdot & \cdot & 1 - (1 - \delta)E & -1 \\
-1 & 2 - E & -1 & \cdot & \cdot \\
\end{pmatrix},
\]  
(17)
and the corresponding determinant is
\[ |M^{(b)}_b| = -2 \tan \frac{\tau}{2} \left[ \sin N\tau - \delta \mathcal{F} \right] \]  
(18)
where
\[ \mathcal{F} = \sin N\tau + \tan \frac{\tau}{2} \cos (N_l - N_r)\tau + \frac{\cos N\tau - \cos (N + 1)\tau}{\sin \tau} \]  
(19)
with \( N_l + N_r + 1 = N \). Similarly we have the critical mass ratio
\[ \delta_c = \frac{N}{(2N_l + 1)(2N_r + 1)} \geq \frac{1}{N} \]  
(20)
where the equality holds unless the length of the chain is odd and \( N_l = N_r \). It is interesting to note that if \( N_l = 0 \), which means that the impurity locates that the end of the chain, (20) should reduce to (16), indicating a self-consistent calculation. Figure 3 shows the critical mass ratio \( \delta_c \) varies with the position \( p \) of the impurity under OBC with the total number \( N = 100 \).
In summary, in the OBC situation, the critical mass ratio $\delta_c$ depends highly on the position of the impurity. If the impurity locates at the end, the critical mass $m_N N_1^2$ is slightly less than half of the perfect atom mass, and tends to $m_2$ for an infinite chain. If the impurity locates at the middle, however, the critical mass ratio relies on its distance from the endpoint, and decreases dramatically from $m_N N_1^2$ to $m_1$ with distance.

4. Vibration frequency and amplitude

4.1. Vibration frequency

It is necessary for us to investigate the frequency and amplitude of the vibration of impurity. For the one impurity case, the frequency can be expressed as [14–16]

$$\omega_f = \frac{\omega_m}{\sqrt{1 - \delta_f^2}} \quad (21)$$

where $\omega_m = \sqrt{E_m \beta / m}$ is the maximum frequency of the local vibration with $E_m = 4$ be the maximum energy of the corresponding perfect monatomic chain, and

$$\delta_f = \frac{m - f m'}{m} = 1 - f \frac{m'}{m} \quad (22)$$

is a fitting parameter that depends on the boundary condition and the position of the impurity. In light of (9), (21) and (22) the factor $f$ can be fitted as

$$f = f_N(\delta) = \frac{1 - \frac{E_m}{E_f}}{1 - \delta} \quad (23)$$

where $E_f = m \omega_f^2 / \beta$ and is also the maximal energy of the total atoms.

Table 1 shows the local vibration energy $E_I$ of the impurity and the corresponding fitting factor $f$ for different boundary conditions, length $N$ and mass ratio $\delta$.

| PBC       | $N = 100$ | $N = 200$ |
|-----------|-----------|-----------|
| $\delta$  | $\delta'$ | $\delta$  | $\delta'$ |
| $E_I$     | $f$       | $E_I$     | $f$       |
| PBC       | $N = 100$ | $N = 200$ |
| $\delta$  | $\delta'$ | $\delta$  | $\delta'$ |
| $E_I$     | $f$       | $E_I$     | $f$       |

In light of (9), (21) and (22) the factor $f$ can be fitted as

$$f = f_N(\delta) = \frac{1 - \frac{E_m}{E_f}}{1 - \delta} \quad (23)$$

where $E_f = m \omega_f^2 / \beta$ and is also the maximal energy of the total atoms.

Table 1 shows the local vibration energy $E_I$ of the impurity and the corresponding fitting factor $f$ for different boundary conditions, length $N$ and mass ratio $\delta$. For any given boundary condition, the local vibration energy $E_I$ relies highly on the mass ratio, but the fitting factor $f$
only slightly varies. Thus, it can be concluded from table 1 that for the PBC the factor $f = 1$ [15], and for the OBC the factor $f = 1$ if the impurity locates at the middle or $f = 2$ if the impurity locates at the end [16]. Our numerical results suggest that splendid accuracy of more than 15 decimal places can be achieved for the fitting factor $f$ as long as the length $N$ of the chain is long enough and/or the mass ratio $\delta$ is large enough.

4.2. Vibration amplitude

The local vibration can be distinguished by the amplitudes of the atoms around the impurity. We will set the length of chain $N = 200$ unless stated otherwise.

Figure 4. The local vibration of impurity with mass ratio $\delta = 0.60$ at $p = 1$ of total length $N = 200$. The critical factor is 0.5012531, and the corresponding vibration frequency is 4.1666667.

Figure 5. The local vibration of impurity with mass ratio $\delta = 0.60$ at $p = 1$ of total length $N = 200$. The critical factor is 0.0050001, and the corresponding vibration frequency is 4.0404040.
Figures 4 and 5 show the occasions where the impurity locates at the end and middle, respectively, of the monatomic linear chain under the OBC. In figure 4 the amplitude of the leftmost impurity is the largest, while the amplitudes of the other atoms oscillate around zero and vanish exponentially along the chain [16], as can be seen from the inset of figure 4. Actually, the amplitudes of the atoms can be analyzed as follows. From the equation of motion of the atoms, we have

\[
\begin{align*}
L_1 &- u_2 = (1 - \delta) \frac{m_2 \omega_I^2}{\beta} u_1, \\
L_2 &- 2u_2 = m_2 \omega_I^2 u_2, \quad k = 2, 3, \ldots, N - 1 \\
L_{N-1} &- u_N = \frac{m_2 \omega_I^2}{\beta} u_N
\end{align*}
\]

where \( \omega_I \) is the frequency of the impurity and can be obtained through (21) approximately. After some basic algebraic operators we get the recurrence form \( \frac{u_{k+1}}{u_k} = -1 - \frac{\delta}{\beta} \), or equivalently

\[
u_k = \nu_1 (-1)^{k-1} \left( \frac{1 - \delta}{\delta} \right)^{k-1} = \nu_1 (-1)^{k-1} e^{-\ln \left( \frac{\delta}{1-\delta} \right)(k-1)}.
\]

Equation (25) holds unless the decay ratio \( t = 1 / \ln \left( \frac{\delta}{1-\delta} \right) > 0 \), i.e. \( \delta > \frac{1}{2} \), which is in accordance with the conclusion in (16).

In figure 5 the amplitudes of the atoms around the impurity reduce gradually, and decay to zero or so at the left and right two endpoints. If the impurity locates at the very middle of the atomic chain, the amplitudes at the left and right sides of the impurity somewhat show symmetry, which is to say that the decay ratios \( t_l \) and \( t_r \) are the same. If not, the decay ratios \( t_l \) and \( t_r \) are different.
Figure 6 shows the amplitude behaviors of the monatomic linear chain with length \( N = 200 \) and \( N = 201 \) under the PBC. For the odd case, the amplitudes will tend to zero or so with the increasing of the distance from the perfect atom to the impurity, and the amplitudes will become zero when the distance is \( [N/2] \). For the even case, however, the amplitudes will only become small but not necessarily be zero for a finite chain. With the increasing of length \( N \) or mass ratio \( \delta \), the amplitudes will become smaller and smaller, and the discrepancy between the even and odd cases will ultimately be eliminated (see the inset).

5. Conclusion

In summary, we show an alternative derivation of the lattice vibration of a one-dimensional monatomic linear chain under open boundary conditions and periodic boundary conditions through the Molinari formula, and give the exact conditions for the emergence of the local vibration mode when one of the atoms is replaced by an impurity. Our derivation is different in that no coupled algebraic equations should be involved, and instead, we shall calculate the determinant of a tridiagonal matrix which can be handled by the Molinari formula. Our method is more general than the above-mentioned traditional method, which can only settle the problem under periodic boundary conditions.

Besides, we give the exact conditions for the emergence of the local vibration mode due to the impurity, which can be measured by the mass ratio \( \delta = \frac{m'}{m} \) where \( m' \) and \( m \) are the mass of the perfect and impurity atoms, respectively. At periodic boundary conditions, the critical mass ratio is 0 or \( \frac{1}{N} \), depending on whether the length \( N \) of the chain is even or odd. At open boundary conditions, the critical mass ratio is \( \frac{N}{2N-1} \) if the impurity locates at the end of the chain, and \( \frac{N}{2N+1} \) if the impurity locates at the middle of the chain. As to the vibration frequency, it can be expressed by \( \omega = \frac{m}{\sqrt{1-\delta^2}} \) depending on the boundary condition and the position of the impurity along the atomic linear chain. The vibration amplitude of the atoms near the impurity decays exponentially with the distance between them.

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Appendix A. Chebyshev polynomial for the determinant of tridiagonal matrix

Let us utilize the Chebyshev polynomial [17] to calculate the determinant of the tridiagonal matrix

\[
T = \begin{pmatrix}
  a & b & b & b \\
  b & a & b & \\
  & b & a & b \\
  b & b & a
\end{pmatrix}
\]  

(A.1)
$T$ is a symmetry circulant matrix, whose $m$th eigenvalue is

$$
\lambda_m = a + b(\omega^m + \omega^{-m}) = a + 2b \cos \frac{2\pi m}{n}
$$

(A.2)

where $\omega = e^{2\pi i/n}$ is the $n$th root of unity. The determinant, therefore, should be

$$
\det(T) = \prod_{m=1}^{n} \lambda_m = \prod_{m=1}^{n} \left[a + 2b \cos \frac{2\pi m}{n}\right] = b^n \prod_{m=1}^{n} \left[\frac{a}{b} + 2 \cos \frac{2\pi m}{n}\right].
$$

(A.3)

By virtue of the definition of the Chebyshev polynomial of the first kind $T_n$, (A.3) is readily

$$
\det(T) = 2(-b)^n \left[T_n\left(-\frac{a}{2b}\right) - 1\right].
$$

(A.4)

Noticing that $T_n(-x) = (-1)^n T_n(x)$ and $T_n(\cos \tau) = \cos n\tau$, we finally reach

$$
\det(T) = 2b^n [(-1)^{n+1} + \cos n\tau].
$$

(A.5)

Similarly, the $m$th eigenvalue of $\bar{T}$ (the two elements at the corner are zero) is

$$
\bar{\lambda}_m = a + b(\bar{\omega}^m + \bar{\omega}^{-m}) = a + 2b \cos \frac{2\pi m}{n+1}
$$

where $\bar{\omega} = e^{i\pi/(n+1)}$ is the $(2n+2)$th root of unity. The determinant in this case is

$$
\det(\bar{T}) = 2b^n U_n\left(\frac{a}{2b}\right)
$$

(A.7)

where $U_n(x)$ is the Chebyshev polynomial of the second kind [17]. Since

$$
U_n(\cos \tau) = \frac{\sin(n+1)\tau}{\sin \tau},
$$

(A.7) is nothing but

$$
\det(\bar{T}) = b^n \frac{\sin(n+1)\tau}{\sin \tau}.
$$

(A.8)

Appendix B. Molinari formula for the determinant of tridiagonal matrix

For any generalized tridiagonal matrix in the form of

$$
T = \begin{pmatrix}
  a_1 & b_1 & & \\
  b_1 & a_2 & b_2 & \\
  & \ddots & \ddots & \ddots \\
  & & b_{n-2} & a_{n-1} & b_{n-1} \\
  & & & b_{n-1} & a_n
\end{pmatrix}
$$

(B.1)

the Molinari formula tells us that its determinant is

$$
\det(T) = 2(-1)^{n+1} \prod_{i=0}^{n-1} b_i + \text{tr} \left[ \prod_{k=1}^{n} \left( a_k - b_{k-1}^2 \right) \right].
$$

(B.2)

In particular, (B.1) will be reduced to the ordinary tridiagonal matrix $T$ when the entry at the corner is zero. We do not intend to repeat the lengthy proof here; readers who are interested in the mathematical details can refer the original papers [11, 12]. Meaningfully, a typical example will be involved in this appendix to demonstrate how to employ the Molinari
formula to calculate the determinant, and the proof of a simplified version of the formula, i.e., 
\[ a_i = a, \quad b_{i-1} = b \quad (i = 1, 2, \ldots, n) \] (see (A.1)) is provided as well for the sake of completeness.

Let us introduce a \( 2 \times 2 \) matrix
\[
M = \begin{pmatrix} d & -1 \\ 1 & 0 \end{pmatrix}
\]
whose \( n \)-order power \( M^n \) will be calculated subsequently. The eigenvalues of \( M \) are \( \lambda_{\pm} = e^{\pm i\tau} \), and the corresponding (unnormalized) eigenvectors are \( v_{\pm} = (e^{\pm i\tau}, 1)^T \) respectively with \( \tau = \arccos(d/2) \). Therefore, the similarity transformation of \( M \) is
\[
M = S\Lambda S^{-1}
\]
where \( \Lambda = \text{diag}(e^{i\tau}, e^{-i\tau}) \), and the transformation matrix is
\[
S = \begin{pmatrix} e^{i\tau} & e^{-i\tau} \\ 1 & 1 \end{pmatrix}
\]
So, we have
\[
M^n = S\Lambda^n S^{-1} = \frac{1}{\sin \tau}\begin{pmatrix} \sin(n + 1)\tau & -\sin(n)\tau \\ \sin(n)\tau & -\sin(n - 1)\tau \end{pmatrix}
\]
When it comes to (A.1), Molinari formula tells us that
\[
\det(T) = 2b^n[(-1)^{n+1} + \cos n\tau]
\]
and
\[
\det(\bar{T}) = b^n\frac{\sin(n + 1)\tau}{\sin \tau},
\]
which are exactly the same as (A.5) and (A.8).

References

[1] Tserpes K I and Silvestre N 2014 Modeling of Carbon Nanotubes, Graphene and their Composites (Berlin: Springer)
[2] Zhu T and Ertekin E 2016 Phonons, localization, and thermal conductivity of diamond nanothreads and amorphous graphene Nano Lett. 16 4763–72
[3] Kittel C 1996 Introduction to Solid State Physics (New York: Wiley)
[4] Ashcroft N W and Mermin N D 1976 Solid State Physics (New York: Holt, Rinehart and Winston)
[5] Grosso G and Parravicini G P 2000 Solid State Physics (New York: Academic)
[6] Jalford J O 1951 I. Normal frequencies of a one-dimensional crystal: II. An approximation to the lattice frequency distribution in isotropic solids J. Chem. Phys. 19 1375–9
[7] Wallis R F 1957 Effect of free ends on the vibration frequencies of one-dimensional lattice Phys. Rev. 105 540–5
[8] Rutherford D E 1947 Some continuant determinants arising in physics and chemistry Proc. R. Soc. Edin. Sect. A 62 229–36
[9] Rutherford D E 1952 Some continuant determinants arising in physics and chemistry—II Proc. R. Soc. Edin. Sect. A 63 232–41
[10] Hira K 2013 A simple evaluation of a determinant in a path integral calculation of a harmonic oscillator propagator Eur. J. Phys. 34 1373–78
[11] Molinari L G 1997 Transfer matrices and tridiagonal-block Hamiltonians with periodic and scattering boundary conditions J. Phys. A: Math. Gen. 30 983–97
[12] Molinari L G 2008 Determinants of block tridiagonal matrices Lin. Algebra Appl. 429 2221–6
[13] Yueh W-G 2005 Eigenvalues of several tridiagonal matrices Appl. Math. E-Notes 5 66–74
[14] Allen P B, Aubin S and Doak R B 2000 Surface phonons and other localized excitations Am. J. Phys. 68 228–31
[15] McCluskey M D 2000 Local vibrational modes of impurities in semiconductors *J. Appl. Phys.* **87** 3593–617

[16] Yu F and Yan X 2014 Resarch on local vibration of a linear monatomic chain with a terminal impurity atom by data induction method *Chin. Coll. Phys.* **33** 4–7 (available in Chinese at http://mall.cnki.net/magazine/Article/DXWL201407002.htm)

[17] Chebyshev polynomials [https://en.wikipedia.org/wiki/Chebyshev_polynomials](https://en.wikipedia.org/wiki/Chebyshev_polynomials)