The shifted eigenvalue problem and phonon frequencies†

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Abstract. It is shown that there is a transformation between the phonon frequencies in certain similar crystals (eg Ge and ZnSe) if it is assumed that the force constants do not vary and only act between nearest neighbours; that is, the effect of varying the masses can be understood in a simple way. We also show how the partial densities of states associated with each mass can be projected out. Finally, using similar techniques, the eigenfrequencies of a simple version of the shell model in Ge are related to an equivalent rigid-ion model.

1. The shifted eigenvalue problem

One of the earliest studies in lattice dynamics was done by Born (1914) and this method may be applied to C, Si and Ge which have the diamond structure with two atoms in each unit cell of an fcc lattice. Born assumed that harmonic forces acted between nearest neighbours only and had a central and a non-central component. Thus the lattice dynamics depends only on two force parameters and the mass. This model is easily generalized to the zinc blende structure where the unit cell contains two different masses. The zinc blende structure is bichromatic so that each atom in the A sublattice has nearest neighbours in the B sublattice and vice versa. The techniques described below can be used to study mass effects in any three-dimensional bichromatic lattice where the local site symmetry is either tetrahedral or cubic and the forces are restricted to act only between the two sublattices.

Simple models are still useful in lattice dynamics even though most attempts to fit experimental data use many parameters to represent the forces between atoms (Herman 1959). In some systems, such as the alkali halides, the introduction of redundant coordinates, as in the shell model, is found to be useful (eg Cochran 1966). Moreover, in studying the vibrations of disordered and particularly amorphous systems, it is often necessary to use simple models (eg Dean 1972) in order to be able to gain some understanding of the effects of disorder or non-crystallinity.

Each atom has three degrees of freedom and so we may define a $3N$ column vector $u_A$ for the A sublattice and a corresponding vector $u_B$ for the B sublattice if $2N$ is the total number of atoms. The eigenfrequencies are given by solutions to equations of the form.

$$\begin{bmatrix} M_A \omega^2 - \gamma & C \\ C^T & M_B \omega^2 - \gamma \end{bmatrix} \begin{bmatrix} u_A \\ u_B \end{bmatrix} = 0$$

(1)

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where $\gamma$ is a proportional to a unit matrix because the local symmetry is tetrahedral at both kinds of site. The matrix $\mathbf{C}$ and its transpose $\mathbf{C}^t$ are real because the potential which connects displacements on different sites is real. The mass dependence is shown explicitly in (1) through the masses of the atoms in the two sublattices $M_A$, $M_B$ and $\gamma$. $\mathbf{C}$

\begin{equation}
(M_A \omega^2 - \gamma) \mathbf{u}_A + \mathbf{C} \mathbf{u}_B = 0 \quad \mathbf{C}^t \mathbf{u}_A + (M_B \omega^2 - \gamma) \mathbf{u}_B = 0.
\end{equation}

If we premultiply the first equation by $\mathbf{C}^t$ and eliminate $\mathbf{C} \mathbf{u}_A$, we obtain

\begin{equation}
(M_A \omega^2 - \gamma)(M_B \omega^2 - \gamma) \mathbf{u}_B = \mathbf{C}^t \mathbf{C} \mathbf{u}_B
\end{equation}

and we see immediately that a scalar quantity $(M_A \omega^2 - \gamma)(M_B \omega^2 - \gamma)$ corresponds to each eigenvalue of the matrix $\mathbf{C}^t \mathbf{C}$. Thus if we change the masses $M_A$, $M_B$ to $M_A'$, $M_B'$ the new eigenfrequencies $\omega_0^2$ are related to the old eigenfrequencies $\omega^2$ through

\begin{equation}
(M_A \omega_0^2 - \gamma)(M_B \omega_0^2 - \gamma) = (M_A \omega^2 - \gamma)(M_B \omega^2 - \gamma).
\end{equation}

A particularly interesting case occurs when $M_A' = M_B' = m$ whence,

\begin{equation}
(m \omega_0^2 - \gamma)^2 = (M_A \omega^2 - \gamma)(M_B \omega^2 - \gamma).
\end{equation}

The phonon dispersion curves for the diamond structure using the Born model are well known (eg Cochran 1966) and are most easily found by Fourier transforming the matrix $\mathbf{C}^t \mathbf{C}$ so that only a 3 $\times$ 3 matrix has to be diagonalized at each point in $k$ space. It is a simple matter to compute the density of states $\rho(\omega^2)$ defined so that $\rho(\omega_0^2) \, d \omega_0^2$ is the number of eigenfrequencies between $\omega_0^2$ and $\omega_0^2 + d \omega_0^2$ by performing a Brillouin zone integration. This computation has been done (von Heimendahl 1973 private communication) for a ratio of central to non-central force constants equal to $\frac{A}{J}$ and is shown in figure 1. It is apparent that this density of states is symmetrical about the mean

![Figure 1. The density of states as a function of frequency squared for the diamond lattice with nearest-neighbour forces with a ratio of central to non-central forces equal to $\frac{A}{J}$.

This is because the unitary transformation $\mathbf{u}_A \rightarrow \mathbf{u}_A$, $\mathbf{u}_B \rightarrow -\mathbf{u}_B$ applied to (1) leaves the eigenvalues invariant, as they are determined by the matrix $\mathbf{C}^t \mathbf{C}$. Therefore to every eigenvalue $\lambda$ of $\mathbf{C}^t \mathbf{C}$ we generate two eigenvalues for $\omega_0^2$ which with equal masses.
are \((\gamma \pm \lambda)/m\); symmetrically placed about the mean \(\gamma/m\). Because translational invariance is assumed in (1), we have

\[0 \leq \omega_0^2 \leq 2\gamma/m.\]  

(6)

In figure 2 we show the more usual \(\rho(\omega_0)\) which is derived from \(\rho(\omega_0^2)\) by the relation

\[\rho(\omega_0) = 2\omega_0 \rho(\omega_0^2).\]  

(7)

![Graph showing \(\rho(\omega_0^2)\) as a function of \(\omega_0^2\).](image)

Figure 2. The same as figure 1 but plotted as a function of frequency instead of frequency squared.

Applying the transformation (5) to the case of unequal masses and assuming \(M_A > M_B\), we can solve the quadratic in \(\omega^2\) to obtain

\[\omega^2 = \left\{\gamma/m \pm \sqrt{[(1 - x^2) (\omega_0^2 - \gamma/m)^2 + (\gamma x/m)^2]^{1/2}} (1 - x^2)^{-1}\right\} \]  

(8)

where the parameter \(x\) is given by

\[x = (M_A - M_B)/(M_A + M_B).\]  

(9)

Without loss of generality, we assume that \(M_A > M_B\) and that the masses of the two unit cells are equal

\[2m = M_A + M_B.\]  

(10)

There are three interesting regions of frequency to consider for the transformation (8):

(i) The elastic properties are determined by the low frequencies and for these

\[\omega^2 = \omega_0^2.\]  

(11)

This is a much more general property and results because the elastic constants are independent of the masses and so because the low-frequency modes are determined only by the elastic constants and the mass of the unit cell, the equality (11) results;

(ii) A gap develops in the spectrum because the square root has its minimum value when \(\omega_0^2 = \gamma/m\) and so there are no modes between

\[\omega^2 = (\gamma/m \pm \gamma x/m)/(1 - x^2),\]

that is, between

\[\omega^2 = \gamma/M_A \quad \text{and} \quad \omega^2 = \gamma/M_B.\]  

(12)
The lower of these two squared frequencies \( \gamma/M_A \) corresponds to the B sublattice being at rest, that is, \( u_B = 0 \) and the higher one \( \gamma/M_B \) to the A sublattice at rest \( u_A = 0 \);

(iii) The maximum frequency occurs when \( \omega_0^2 = 2\gamma/m \) and so we have

\[
(\omega^2)^{\text{max}} = \frac{2\gamma/m}{1 - x^2} = \gamma \left( \frac{1}{M_A} + \frac{1}{M_B} \right)
\]

(13)

which depends on the reduced mass of the unit cell and corresponds to a \( k = 0 \) optic mode in which the two sublattices move against each other so that the centre of mass remains fixed. These features may be seen in figure 3 for values of the masses appropriate to ZnSe. The transformed density of states is easily found from the transformation (8)

\[
\rho(\omega) = \rho(\omega_0) (\omega_0/\omega_0) [\omega^2(1 - x^2) - \gamma/m] / (\omega_0^2 - \gamma/m).
\]

(14)

As the mass difference increases so the gap in the spectrum increases. The observant reader will notice the similarities between the preceding discussion and the longitudinal vibrations of the diatomic linear chain with nearest-neighbour forces (eg Kittel 1967). Thus it is not unexpected that the eigenfrequencies are given by a matrix of the form (1) in that case also. Two-dimensional examples of bichromatic lattices such as the square net and the honeycomb lattice also come to mind. We may therefore conclude that mass effects on the eigenfrequencies arise from rather general considerations and do not depend on geometry and dimensionality.
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The Born model for the diamond structure has some rather unfortunate degeneracies which are most easily seen in $k$ space. For the case of equal masses, one of these is the mean eigenfrequency $\omega_0 = \gamma/m$ which is degenerate along certain lines. Because there is a vanishingly small amount of phase space associated with these lines, the density of states goes to zero at the mean eigenfrequency as

$$\rho(\omega_0) \sim |\omega_0^2 - \gamma/m| \ln |\omega_0^2 - \gamma/m|.$$  \hspace{1cm} (15)

In the case of unequal masses, the mean frequency $\omega_0$ is transformed into the frequencies of the inner band edges and the prefactor in (15) is cancelled by a similar factor in (14) so that a weak logarithmic divergence is displayed in figure 3.

2. Partial density of states

By re-examining equation (2) we can easily evaluate the partial densities of states for the two sublattices defined as

$$f_A = M_A |u_A|^2 / [M_A |u_A|^2 + M_B |u_B|^2]$$  \hspace{1cm} (16)

so that $f_A + f_B = 1$.

The mass factors are necessary in the definition of $f_A$ so that the partial density of states may be correctly projected out. This can be seen from the matrix (1).

Using (2) and (3), we see that

$$f_A = [1 + (M_B/M_A)(m\omega_0^2 - \gamma)^2/(M_B\omega^2 - \gamma)^2]^{-1}$$  \hspace{1cm} (17)

which may be simplified using (5)

$$f_A = \frac{1}{2}[1 - \chi/(m(1 - \chi^2)\omega^2 - \gamma)].$$  \hspace{1cm} (18)

The factors $f_A, f_B$ project out the partial densities from $\rho(\omega)$ for the two sublattices. These partial densities of states are also shown in figure 3. In the vicinity of the gap it will be noticed that the weak logarithmic divergence at the lower frequency is associated with the heavy mass and at the higher frequency with the light mass. This is to be expected following the discussion in the previous section.

3. The shell model

The shell model in lattice dynamics introduces extra electronic degrees of freedom (see Cochran 1966). These degrees of freedom do not lead to extra modes as the electron mass is neglected relative to the nuclear mass. The electron shells are assumed to be rigid and spherical with the displacement of the centre from equilibrium described by a vector $v$. The interaction between the shells is the same as the interaction between the ions in the rigid-ion model described previously and dependent on $\gamma$ and $C$. All long-range Coulomb forces are neglected. The potential between the shell and ion must be spherically symmetric because of the local tetrahedral symmetry and so depend on a single force parameter. Therefore we have the following equations for the eigenfrequencies,

$$\begin{bmatrix}
    m\omega^2 - s & s & 0 & 0 \\
    s & -\gamma - s & 0 & C \\
    0 & 0 & m\omega^2 - s & s \\
    0 & C^2 & s & -\gamma - s
\end{bmatrix}
\begin{bmatrix}
u_A \\
u_A \\
u_B \\
u_B
\end{bmatrix} = 0.$$  \hspace{1cm} (19)
In these equations $u_A, u_B$ have the same meaning as before; $v_A, v_B$ are the associated shell degrees of freedom and $s$ is proportional to a unit matrix. If we write out the equations as in (2) and eliminate $v_A, v_B, u_B$, we obtain,

$$[(mw^2 - \gamma) + \gamma mo^2/s^2]/[1 - mo^2/s^2] u_B = C^T C u_B.$$  \hspace{1cm} (20)

Comparing (20) with (3) and putting both masses equal to $m$ and replacing $\omega$ by $\omega_0$ in (3) we obtain

$$[(mw^2 - \gamma) + \gamma mo^2/s^2]/[1 - mo^2/s^2] = m\omega_0^2 - \gamma$$ \hspace{1cm} (21)

which leads to

$$\omega^2 = \omega_0^2/(1 + mo^2/s).$$ \hspace{1cm} (22)

The result (22) shows that all the rigid-ion frequencies $\omega_0$ are renormalized in a simple, monotonic way. As is well known, the shell model is capable of accounting for the very flat transverse acoustic branch in Si and Ge without altering the elastic constants as given by the rigid-ion model. These features can be seen in the transformation (22). The density of states also transforms in a simple way

$$\rho(\omega) = \rho(\omega_0)(\omega_0/\omega)^3.$$ \hspace{1cm} (23)

Although the simple shell model described here does not have as many parameters as some others and so cannot give such a precise fit to the measured phonon frequencies; this simplicity may be an advantage when a simple model is needed as, for example, in the study of the vibrations of amorphous Si and Ge.

Acknowledgment

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References


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