1. Quantum Mechanical Treatment

Our starting point is the Schrödinger wave equation:

\[
\left(-\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial r_i^2} + U(\vec{r}_1, \ldots, \vec{r}_N)\right)\Psi(\vec{r}_1, \ldots, \vec{r}_N) = E \Psi(\vec{r}_1, \ldots, \vec{r}_N),
\]

(1.1)

where \(N\) is the number of atoms in the molecule, \(m_i\) is the mass of the \(i\)’th atom, and \(U(\vec{r}_1, \ldots, \vec{r}_N)\) is the effective potential for the nuclear motion, e.g., as is obtained in the Born-Oppenheimer approximation.

If the amplitude of the vibrational motion is small, then the vibrational part of the Hamiltonian associated with Eq. (1.1) can be written as:

\[
H_{\text{vib}} \approx -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \Delta_i^2} + U_0 + \frac{1}{2} \sum_{i,j=1}^{N} \hat{K}_{i,j} \Delta_i \Delta_j,
\]

(1.2)

where \(U_0\) is the minimum value of the potential energy, \(\Delta_i \equiv \vec{r}_i - \vec{R}_i\), \(\vec{R}_i\) is the equilibrium position of the \(i\)’th atom, and \(\hat{K}_{i,j}\) is the matrix of (harmonic) force constants. Henceforth, we will shift the zero of energy so as to make \(U_0 = 0\). Note that in obtaining Eq. (1.2), we have neglected anharmonic (i.e., cubic and higher order) corrections to the vibrational motion.

The next and most confusing step is to change to matrix notation. We introduce a column vector containing the displacements as:

\[
\Delta \equiv [\Delta_1^x, \Delta_1^y, \Delta_1^z, \ldots, \Delta_N^x, \Delta_N^y, \Delta_N^z]^T,
\]

(1.4)

where "\(T\)" denotes a matrix transpose. Similarly, we can encode the force constants or masses into \(3N \times 3N\) matrices, and thereby rewrite Eq. (1.2) as

\[
H_{\text{vib}} = -\frac{\hbar^2}{2} \left( \frac{\partial}{\partial \Delta} \right)^\dagger \mathbf{M}^{-1} \left( \frac{\partial}{\partial \Delta} \right) \Delta + \frac{1}{2} \Delta^\dagger \mathbf{K} \Delta,
\]

(1.5)

where all matrix quantities are emboldened, the superscript "\(\dagger\)" denotes the Hermitian conjugate (matrix transpose for real matrices), and where the mass matrix, \(\mathbf{M}\), is a diagonal matrix with the masses of the given atoms each appearing three times on the diagonal.

The Hamiltonian given by Eq. (1.5) is the generalization of the usual harmonic oscillator Hamiltonian to include more particles and to allow for "springs" between arbitrary particles. Unless \(\mathbf{K}\) is diagonal (and it usually isn’t) Eq. (1.5) would seem to suggest that the vibrational problem for a polyatomic is non-separable (why?); nonetheless, as we now show, it can be separated. This is first shown using using the quantum mechanical framework we’ve just set up.
Later, we will discuss the separation using classical mechanics. This is valid since, for harmonic oscillators, you get the same result for the vibration frequencies.

We now make the transformation \( \Delta_i \rightarrow m_i^{-1/2} \hat{\Delta}_i \), which allows Eq. (1.5) to be reexpressed in the new coordinates as

\[
H_{vib} = -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \Delta^2} \right) \left( \frac{\partial}{\partial \Delta} \right) + \frac{1}{2} \Delta^\dagger \tilde{K} \Delta, \tag{1.6}
\]

where

\[
\tilde{K} \equiv M^{-1/2} K M^{-1/2}. \tag{1.7}
\]

Since the matrix \( \tilde{K} \) is Hermitian (or symmetric for real matrices), it is possible to find a unitary (also referred to as an orthogonal matrix for real matrices) matrix which diagonalizes it; i.e., you can find a matrix \( P \) which satisfies

\[
P^\dagger \tilde{K} P = \lambda \quad \text{or} \quad \tilde{K} = P \lambda P^\dagger, \tag{1.8}
\]

where \( \lambda \) is diagonal (with real eigenvalues) and where

\[
P \ P^\dagger = 1 \tag{1.9}
\]

where \( I \) is the identity matrix. Note that \( P \) is the unitary matrix who’s columns are the normalized eigenvectors. (See a good quantum mechanics book or any linear algebra text for proofs of these results).

We now make the transformation

\[
\Delta \rightarrow P \Delta \tag{1.10}
\]

in Eq. (1.5). This gives

\[
H_{vib} = -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \Delta^2} \right) \left( \frac{\partial}{\partial \Delta} \right) + \frac{1}{2} \Delta^\dagger \tilde{\lambda} \Delta, \tag{1.11}
\]

Finally, Eq. (1.8) allows us to cancel the factors of \( P \) in this last equation and write

\[
H_{vib} = \sum_{i=1}^{3N} \left( -\frac{1}{2} \frac{\hbar^2}{\lambda_i^2} \frac{\partial^2}{\partial \Delta_i^2} + \frac{1}{2} \lambda_i \Delta_i^2 \right). \tag{1.12}
\]

Thus the two transformations described above have separated the Hamiltonian into \( 3N \) uncoupled harmonic oscillator Hamiltonians, and are usually referred to as a normal mode transformation. Remember that in general the normal mode coordinates are not the original displacements from the equilibrium positions, but correspond to collective vibrations of the molecule.

2. Normal Modes in Classical Mechanics

The starting point for the normal mode analysis in classical mechanics are Newton’s equations for a system of coupled harmonic oscillators. Still, using the notation that led to Eq. (1.12), we can write the classical equations of motion as:

\[
M \dot{\Delta}(t) = -K \Delta(t), \tag{2.1}
\]

where components of the left-hand-side of the equation are the rates of change of momentum of the nuclei, while the right-hand-side contains the harmonic forces.
Since we expect harmonic motion, we’ll look for a solution of the form:

\[ \Delta(t) = \cos(\omega t + \phi)Y, \]

where \( \phi \) is an arbitrary phase shift. If Eq. (2.2) is used in Eq. (2.1) it follows that:

\[ (M\omega^2 - K)Y = 0, \]

where remember that \( Y \) is a column vector and \( M \) and \( K \) are matrices. We want to solve this homogeneous system of linear equations for \( Y \). In general, the only way to get a nonzero solution is to make the matrix \( [M\omega^2 - K] \) singular; i.e., we must set

\[ \det(M\omega^2 - K) = \det(\omega^2 - M^{-1/2}KM^{-1/2})\det(M) = 0. \]

Since, \( \det(M) = (M_1M_2\ldots M_N)^3 \neq 0 \) we see that the second equality is simply the characteristic equation associated with the eigenvalue problem:

\[ \tilde{K}u = \lambda u, \]

with \( \lambda \equiv \omega^2 \) and with \( \tilde{K} \) given by Eq. (2.7) above. The remaining steps are equivalent to what was done quantum mechanically.

3. Force Constant Calculations

Here is an example of a force constant matrix calculation. We will consider a diatomic molecule, where the two atoms interact with a potential of the form:

\[ U(r_1, r_2) \equiv \frac{1}{2} K \left( |r_1 - r_2| - R_0 \right)^2; \]

i.e., a simple Hookian spring. It is easy to take the various derivatives indicated in the preceding sections; here, however, we will explicitly expand the potential in terms of the atomic displacements, \( \Delta_i \). By writing, \( r_i = R_i + \Delta_i \) (where \( R_i \) is the equilibrium position of the \( i \)’th nucleus), Eq., (3.1) can be rewritten as:

\[ U(r_1, r_2) = \frac{1}{2} K \left( R_{12}^2 + 2R_{12} \cdot (\Delta_1 - \Delta_2) + |\Delta_1 - \Delta_2|^2 \right)^{1/2} - R_0 \right)^2, \]

where \( R_{12} \equiv R_1 - R_2 \). Clearly, the equilibrium will have \( |R_{12}| = R_0 \). Moreover, we expect that the vibrational amplitude will be small, and thus, the terms in the \( \Delta \)’s in the square root in Eq. (3.2) will be small compared with the first term. The Taylor expansion of the square root implies that

\[ \sqrt{A + B} = \sqrt{A} + \frac{B}{2\sqrt{A}} + \ldots, \]

we can write

\[ U(r_1, r_2) = \frac{1}{2} K \left( R_{12}^2 + \frac{2R_{12} \cdot (\Delta_1 - \Delta_2) + |\Delta_1 - \Delta_2|^2}{2R_{12}} - R_0 \right)^2, \]

which can be rewritten as

\[ U(r_1, r_2) = \frac{1}{2} K \left( \hat{R}_{12} \cdot (\Delta_1 - \Delta_2) \right)^2, \]
where the \( \hat{\cdot} \) denotes a unit vector and where all terms smaller than quadratic in the nuclear displacements have been dropped. If the square is expanded, notice the appearance of cross terms in the displacements of 1 and 2.

It is actually quite simple to finish the normal mode calculation in this case. To do so, define the equilibrium bond to point in along the \( x \) axis. Equation (3.5) shows that only \( x \)-components of the displacements cost energy, and hence, there will no force in the \( y \) or \( z \) directions (thereby resulting in 4 zero eigen-frequencies). For the \( x \) components, Newton’s equations become:

\[
\begin{pmatrix} m_1 & 0 \\ 0 & m_2 \end{pmatrix} \ddot{\Delta}_x^1 = - \begin{pmatrix} K & -\hat{K} \\ -\hat{K} & K \end{pmatrix} \Delta_x^1
\]

where \( m_i \) is the mass of the \( i \)'th nucleus. This in turn leads to the following characteristic equation for the remaining frequencies:

\[
0 = \det \left[ \begin{pmatrix} m_1 & 0 \\ 0 & m_2 \end{pmatrix} \omega^2 - \begin{pmatrix} K & -\hat{K} \\ -\hat{K} & K \end{pmatrix} \right]
\]

\[
= (m_1 \omega^2 - K)(m_2 \omega^2 - K) - K^2
\]

\[
= \omega^2(\mu \omega^2 - K),
\]

where \( \mu \equiv m_1 m_2/(m_1 + m_2) \) is the reduced mass. Thus we pick up another zero frequency and a nonzero one with \( \omega = \sqrt{K/\mu} \), which is the usual result. (Note that we don’t count \( \pm \) roots twice--WHY?).

4. Normal Modes in Crystals

The main result of the preceding sections is that the characteristic vibrational frequencies are obtained by solving for eigenvalues, cf., Eq. (2.5). For small to mid-size molecules this can be done numerically, on the other hand, this is not practical for crystalline solids where the matrices are huge \((3N \times 3N)\) with \( N \sim O(N_A) \)!

Crystalline materials differ from small molecules in one important aspect; they are periodic structures made up of identical unit cells; specifically, each unit cell is placed at

\[
\vec{R} = n_1 \hat{a}_1 + n_2 \hat{a}_2 + n_3 \hat{a}_3,
\]

where \( n_i \) is an integer and \( \hat{a}_i \) is a primitive lattice vector. The atoms are positioned within each unit cell at positions labeled by an index, \( \alpha \). Thus, the position of any atom in entire crystal is determined by specifying \( \vec{R} \) and \( \alpha \). Hence, Eq. (2.5) can be rewritten as

\[
\lambda u_{\alpha R} = \sum_{R'} \sum_{R', \alpha'} \vec{K}_{R, \alpha; R', \alpha'} u_{R', \alpha'}.
\]

The periodicity of the lattice implies that only the distance between unit cells can matter; i.e., \( \vec{K}_{R, \alpha; R', \alpha'} = \vec{K}_{R; R', \alpha; \alpha'} \), and this turns Eq. (4.2) into a discrete convolution that can be simplified by introducing a discrete Fourier transform, i.e., we let

\[
\tilde{u}_{k, \alpha} = \sum_{\vec{R}} e^{ik \cdot \vec{R}} u_{\alpha R}.
\]
When applied to both sides of Eq. (2.5), this gives

\[ \lambda \tilde{u}_k = \sum_{\alpha} \tilde{K}_{k,\alpha,\alpha'} \tilde{u}_{k',\alpha}, \]  

(4.4)

where

\[ \tilde{K}_{k,\alpha,\alpha'} = \sum_{R} e^{iR \cdot \tilde{K}} R \tilde{K}_{R,\alpha,\alpha'}. \]  

(4.5)

The resulting eigenvalue problem has rank \( \mathcal{N} \), where \( \mathcal{N} \) is the number of atoms in a unit cell, and is easily solved numerically.

We haven’t specified the values for the \( \tilde{k} \)’s. It turns out that a very convenient choice is to use \( \tilde{k} \)’s expressed in terms of the so-called reciprocal lattice vectors, \( \tilde{G} \), i.e.,

\[ \tilde{G} \equiv m_1 \tilde{b}_1 + m_2 \tilde{b}_2 + m_3 \tilde{b}_3, \]  

(4.6)

where the \( m_i \)’s are integers, and where the reciprocal lattice basis vectors are defined as†

\[ \tilde{b}_1 = 2\pi \frac{\tilde{a}_2 \times \tilde{a}_3}{|\tilde{a}_1 \cdot (\tilde{a}_2 \times \tilde{a}_3)|}, \quad \tilde{b}_2 = 2\pi \frac{\tilde{a}_3 \times \tilde{a}_1}{|\tilde{a}_2 \cdot (\tilde{a}_3 \times \tilde{a}_1)|}, \quad \text{and} \quad \tilde{b}_3 = 2\pi \frac{\tilde{a}_1 \times \tilde{a}_2}{|\tilde{a}_3 \cdot (\tilde{a}_1 \times \tilde{a}_2)|}. \]  

(4.7)

Note the following:

a) The denominators appearing in the definitions of the \( \tilde{b}_i \) are equal; i.e.,

\[ |\tilde{a}_1 \cdot (\tilde{a}_2 \times \tilde{a}_3)| = |\tilde{a}_2 \cdot (\tilde{a}_3 \times \tilde{a}_1)| = |\tilde{a}_3 \cdot (\tilde{a}_1 \times \tilde{a}_2)| = \nu_{cell}, \]  

(4.8)

where \( \nu_{cell} \) is the volume of the unit cell. The volume of the reciprocal lattice unit cell is \((2\pi)^3/\nu_{cell}\).

b) By construction,

\[ \tilde{a}_i \cdot \tilde{b}_j = 2\pi \delta_{i,j}, \]  

(4.9)

where \( \delta_{i,j} \) is a Kronecker-\( \delta \).

c) The real and reciprocal lattices need not be the same, even ignoring how the basis vectors are normalized; e.g., they are for the SCC, but the reciprocal lattice for the BCC lattice is a FCC lattice.

d) For any lattice vector, \( \tilde{R} \), and reciprocal lattice vector, \( \tilde{G} \),

\[ e^{i \tilde{R} \cdot \tilde{G}} = e^{2\pi i (m_1 n_1 + m_2 n_2 + m_3 n_3)} = 1, \]  

(4.10)

cf. Eqs. (4.1), (4.6), and (4.9). Hence, adding any reciprocal a lattice vector to the \( \tilde{k} \) in Eq. (4.4) changes nothing, and so, we restrict \( \tilde{k} \) to what is known as the First Brillouin Zone; specifically,

\[ \tilde{k} = k_1 \tilde{b}_1 + k_2 \tilde{b}_2 + k_3 \tilde{b}_3, \]  

(4.11)

where \( k_i \equiv m_i / \mathcal{N}_i \) with \( m_i = 0, 1, 2, \ldots, \mathcal{N}_i - 1 \). Note that \( \mathcal{N}_1 \mathcal{N}_2 \mathcal{N}_3 = \mathcal{N} \), the total number of

† Strictly speaking, in obtaining Eq. (4.5) we have assumed some special properties of the lattice. We don’t use a finite lattice, rather one that obeys periodic boundary conditions (see below).

cells in the crystal. The $N_i$'s are the number of cells in the $\mathbf{a}_i$ direction. With this choice, consider

$$\frac{1}{N} \sum_{\mathbf{k}} e^{-i \mathbf{k} \cdot \mathbf{r}_{k,a}} = \frac{1}{N} \sum_{\mathbf{k}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}_0)} u_{\mathbf{R},a} = \sum_{\mathbf{R}} u_{\mathbf{R},a} \prod_{i=1}^{3} \left( \frac{1}{N_i} \sum_{m_i=0}^{N_i-1} e^{2 \pi i m_i (n_i'-n_i)/N_i} \right).$$  \hspace{1cm} (4.12)

The sums in parenthesis are geometric series and give

$$\frac{1}{N} \sum_{m_i=0}^{N_i-1} e^{2 \pi i m_i (n_i'-n_i)/N_i} = \frac{1}{N_i} \left( e^{2 \pi i (n_i'-n_i)/N_i} - 1 \right) = \delta_{n_i',n_i},$$ \hspace{1cm} (4.13)

which when used in Eq. (4.12) shows that

$$\frac{1}{N} \sum_{\mathbf{k}} e^{-i \mathbf{k} \cdot \mathbf{r}_{k,a}} = u_{\mathbf{R},a}.$$ \hspace{1cm} (4.14)

The sums over $\mathbf{k}$ are really sums over the $m_i$'s, and thus, $k_i$ hardly changes as we go from $m_i \rightarrow m_i + 1$ for large $N_i$, cf. Eq. (4.11). This allows the sums over $m_i$ to be replaced by integrals; i.e.,

$$\sum_{\mathbf{k}} \ldots \rightarrow \prod_{i=1}^{3} \int_0^{N_i-1} dm_i \ldots = \frac{V}{(2\pi)^3} \int \int \int d\mathbf{k},$$ \hspace{1cm} (4.15)

where $V = N \nu_{cell}$ is the volume of the system.

The main goal of this discussion is to obtain the vibrational density of states. By using Eq. (4.15), it is easy to show that

$$g(\omega) = \frac{V}{(2\pi)^3} \int \int \int d\mathbf{k} \delta(\omega - \omega(\mathbf{k})), \hspace{1cm} (4.16)$$

where $\delta(x)$ is the Dirac $\delta$-function. Once the frequencies are known, it is relatively easy to numerically bin them by frequency as a function of $\mathbf{k}$.

5. Normal Modes in Crystals: An Example

Consider a crystal with one atom of mass $m$ per unit cell and nearest neighbor interactions of the type considered in Sec. 3. Newton’s equations of motion for this atom become

$$m \ddot{x}_{0,0,0} = K [\dot{\mathbf{e}}_x (\Delta_{1,0,0,0} + \Delta_{1,0,0,0} - 2\Delta_{0,0,0,0}) + \dot{\mathbf{e}}_y (\Delta_{0,1,0,0} + \Delta_{0,1,0,0} - 2\Delta_{0,0,0,0})$$

$$+ \dot{\mathbf{e}}_z (\Delta_{0,0,1,0} + \Delta_{0,0,1,0} - 2\Delta_{0,0,0,0})],$$ \hspace{1cm} (5.1)

where $\dot{\mathbf{e}}_i$ is a unit vector in the $i$ direction. Note that this model implies that vibrations in the $x$, $y$, $z$ directions are separable. By using this in Eq. (4.5) we see that

\footnote{The more common choice for the range of the $m_i$'s is $m_i = -N_i/2, \ldots, 0, \ldots, N_i/2$, which, cf. Eq. (4.11), means that $-1/2 \leq k_i \leq 1/2$.}
\[ \tilde{K}_k = -4\omega_0^2 \begin{pmatrix} \sin^2(k_1\pi) & 0 & 0 \\ 0 & \sin^2(k_2\pi) & 0 \\ 0 & 0 & \sin^2(k_3\pi) \end{pmatrix}, \quad (5.2) \]

where \( \omega_0 \equiv (K/m)^{1/2} \) and where the identity, \( 1 - \cos(x) = 2\sin^2(x/2) \) was used. Since \( \tilde{K}_k \) is already diagonal, we see that \( \omega_i(k) = 2\omega_0 \sin(k_i\pi), \ i = 1, 2, 3 \), which is also the result for a one dimensional chain (as was expected, given the separability of the vibrations in the \( x, y, \) and \( z \) directions). The normal mode is just \( \tilde{e}_i \), which shows that our model potential is too simple. Consider the first eigen-vector. It corresponds to an arbitrary displacement in the \( x \) direction, with an eigenvalue that is independent of \( k_y \) and \( k_z \). When \( k_x = 0 \) we don’t get a single zero frequency, as expected, but one for any of the \( N_y, N_z \) values of \( (k_y, k_z) \). Thus, with \( 3N^{2/3} \) zero frequencies, not 6, the crystal is unstable!

The problem is easily fixed by modifying the interaction potential, i.e., we replace Eq. (3.5) by

\[ U \equiv \frac{K}{2} (\tilde{\Delta}_1 - \tilde{\Delta}_2)^2, \quad (5.3) \]

which is invariant under rigid translations and rotations, and allows us to rewrite Eq. (5.1) as

\[ m\ddot{\Delta}_{0,0,0} = K(\tilde{\Delta}_{1,0,0} + \tilde{\Delta}_{-1,0,0} - 2\tilde{\Delta}_{0,0,0} + \tilde{\Delta}_{0,1,0} + \tilde{\Delta}_{0,-1,0} - 2\tilde{\Delta}_{0,0,1} + \tilde{\Delta}_{0,0,1} - 2\tilde{\Delta}_{0,0,0}). \quad (5.4) \]

With this, it follows that

\[ \tilde{K}_k = -4\omega_0^2 [\sin^2(k_1\pi) + \sin^2(k_2\pi) + \sin^2(k_3\pi)]1, \quad (5.5) \]

where \( \mathbf{1} \) is a \( 3 \times 3 \) identity matrix and where we have expressed \( \tilde{K} \) in terms of the reciprocal lattice basis vectors, cf. Eq (5.11). The triply degenerate vibrational frequencies are simply

\[ \omega_i(k) = 2\omega_0 [\sin^2(k_1\pi) + \sin^2(k_2\pi) + \sin^2(k_3\pi)]^{1/2}. \quad (5.6) \]

If all the \( k_i \rightarrow 0 \), Eq. (5.6) becomes \( \omega(k) \sim 2\omega_0 k\pi \), where \( k \equiv (k_1^2 + k_2^2 + k_3^2)^{1/2} \) which is the expected linear dispersion law for long wavelength, acoustic vibrations. Some constant frequency surfaces in the First Brillouin Zone are shown in Figs. 5.1-5.3.
Fig. 5.1. A constant normal mode frequency surface for $\omega/\omega_0 = 1$. The reciprocal lattice basis was used which need not be orthogonal (although it is for the SCC lattice). Also note that we've switched to the other definition of the first Brillouin zone, with $-1/2 \leq k_i \leq 1/2$. The surface is roughly spherical, as expected for long wavelength acoustic phonons.

Fig. 5.2. As in Fig. 5.1 but with $\omega/\omega_0 = 2$. Notice the $C_4$ axes through the centers of any of the unit cell faces.

Fig. 5.3. As in Fig. 5.1 but with $\omega/\omega_0 = 3$.

Normal mode frequencies for this model were computed numerically for a uniform sample of $k_i$'s in the First Brillouin Zone and binned in order to get the vibrational density of states as shown in Fig. 5.4.
Fig. 5.4. Vibrational density of states for the isotropic model defined by Eq. (5.3). Any single atom per unit cell lattice will give the same result. The data was obtained by numerically binning the frequencies in the First Brillouin Zone. Note that the maximum frequency for this model is $2\sqrt{3}\omega_0$.

By noting that

$$\delta(f(x)) = \sum_i \delta(x - x_i) \left| \frac{df(x_i)}{dx} \right|,$$

(5.7)

where $f(x)$ has zeros at $x = x_i$, $i = 1, \ldots$, and that

$$\delta(x) = \int_{-\infty}^{\infty} ds \frac{e^{ixs}}{2\pi},$$

(5.8)

we can rewrite Eq. (4.16) as

$$\frac{g(\omega)}{3N} = 2\omega \int_0^1 dk_1 \int_0^1 dk_2 \int_0^1 dk_3 \delta(\omega^2 - \omega^2(k))$$

$$= \frac{\omega}{\pi} \int_{-\infty}^{\infty} ds \int_0^1 dk_1 \int_0^1 dk_2 \int_0^1 dk_3 e^{is(\omega^2 - \omega^2(k))}$$

$$= \frac{\omega}{\pi} \int_{-\infty}^{\infty} ds e^{is\omega^2} \Phi^3(s),$$

where the extra factor of 3 is due to the triple degeneracy of each mode and where

$$\Phi(s) \equiv \int_0^1 dk e^{-4i\omega_0^2 s \sin^2(\pi k)}$$

When we use Eq. (5.7) for the frequencies, it follows that the wavevector integrations separate and
\[ g(\omega) = 2V \omega \int_{-\infty}^{\infty} ds \frac{e^{is\omega^2}}{2\pi} \Phi^3(s), \]  

(5.9)

where

\[ \Phi(s) \equiv \int \frac{dk_1}{2\pi} e^{-is4a_0^2 \sin^2(\pi k_1)} = \int_{-\infty}^{\infty} dz \ e^{2\omega_0^2 is \cos(z)} \]

\[ = \frac{e^{-2\omega_0^2 is}}{2\pi^2} \int_{-1}^{1} dz \ \frac{e^{2\omega_0^2 isz}}{(1 - z^2)^{1/2}} = \frac{e^{-2\omega_0^2 is}}{2\pi} J_0(2\omega_0^2 s), \]  

(5.10)

where \( J_0(x) \) is a Bessel function of the first kind. When this is used in Eq. (5.10), we see that

\[ g(\omega) = \frac{2V \omega}{(2\pi)^4} \int_{-\infty}^{\infty} ds \ e^{is(\omega^2 - 6a_0^2)} J^3_0(2\omega_0^2 s) \]  

(5.11)

*The integral leading to the last equality can be found in I.S. Gradsheyn and I.M. Ryzhik, *Table of Integrals, Series, and Products*, A. Jeffrey editor, (Academic Press, 1980), Eq. (3.387.2) on p. 321.*