

Chapter 1

Lattice Dynamics in the Harmonic Approximation

We start our exploration of the Green's function approach by considering the problem of a lattice of interacting vibrating atoms. Within the harmonic approximation this represents perhaps the simplest type of many-body problem. By transforming to normal-mode coordinates the hamiltonian can be reduced to that of a set of independent oscillators and can thus be diagonalized exactly. But such exact closed solutions can only be obtained in quantum mechanics in exceptional cases, and it is therefore worth studying this problem by means of a more general formalism which can also be applied to more complicated cases, such as the important but much more difficult problem of the lattice dynamics of an *anharmonic* crystal. This is one reason for studying the harmonic problem by means of Green's functions. Another is that the Green's function approach provides a unified systematic method for calculating various quantities of physical interest. Thus we shall see that it gives the ground state energy of the system, or—more generally—the free energy at non-zero temperature, from which the thermodynamic properties such as the specific heat can be obtained.

In addition to these equilibrium properties, Green's functions also provide information on the excitation energies of a system. For example, scattering processes correspond to excitations in which one particle is added to the system, and we shall consider the scattering of thermal neutrons by the lattice vibrations as an example of this. There is also an important class of excitations in which the particle number is conserved; the theory of linear response to an externally applied field describes such excitations and, as we shall see in later chapters, provides expressions for dielectric response functions, electrical conductivities and magnetic susceptibilities in terms of appropriately defined Green's functions. Green's functions thus make it possible to evaluate measurable thermodynamic and transport properties by studying the response of a system to simple perturbations. This approach is particularly important for

interacting many-particle systems, where the complete set of wave functions and energy levels is highly complex but is not in fact needed for studying properties related to experiment.

In the first three chapters we use the harmonic lattice as an exactly soluble example to study and compare the principal methods for calculating Green's functions. The physical phenomena produced by the interaction between atoms in this case are the propagating modes—excitation energy is handed on from one atom to the next so as to produce traveling sound waves (quantized as phonons). We shall find later that in more complicated cases also there exist excitations which take the form of sets of coupled oscillators—plasmon excitations in the case of an electron gas with Coulomb interactions (Chap. 6), and spin waves in the case of an insulating magnet (Chap. 8). Thus the phonon Green's function serves also as a prototype for studying a number of other interacting systems of interest in solid state physics.

1.1 THE GROUND STATE ENERGY

We consider the hamiltonian

$$H = \sum_i \frac{\mathbf{p}_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} V(\mathbf{X}_i - \mathbf{X}_j), \quad (1.1.1)$$

which describes a simple lattice composed of N identical interacting atoms of mass M situated at the points \mathbf{X}_i ($i = 1, 2, \dots, N$). It is assumed that the potential energy V is a two-body potential which depends only upon the relative positions of pairs of atoms. We write $\mathbf{X}_i = \mathbf{R}_i + \mathbf{u}_i$, where \mathbf{R}_i is an undisplaced lattice point and the lattice displacement \mathbf{u}_i is assumed to be small. In the harmonic approximation V is expanded in powers of the \mathbf{u}_i as far as second-order terms. Since the expansion is about the equilibrium configuration the coefficients of the linear terms are zero, and the expansion is

$$H = \sum_i \frac{\mathbf{p}_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} \frac{1}{2!} (u_i^\alpha - u_j^\alpha)(u_i^\beta - u_j^\beta) \nabla^\alpha \nabla^\beta V, \quad (1.1.2)$$

where u_i^α is a cartesian component of \mathbf{u}_i .

To separate out the interaction between different atoms we rewrite

the potential energy term as

$$\frac{1}{4} \sum_{i \neq j} \sum_{\alpha\beta} \{ (u_i^\alpha u_i^\beta + u_j^\alpha u_j^\beta) - (u_j^\alpha u_i^\beta + u_j^\beta u_i^\alpha) \} \nabla^\alpha \nabla^\beta V,$$

where we have separated the terms which involve only the displacements of a single atom i from the interaction terms which depend on the displacements of two different atoms i and j . If the interaction terms are neglected we have the *Einstein model* of lattice vibrations, in which each atom vibrates independently with constant frequency (Ω_0 , say) in the potential well of its neighbors' force fields. Because of the interactions there is a tendency for the motion of adjacent atoms to be correlated, and this leads to a change in the Einstein frequencies of the system.

We treat the Einstein oscillators as the unperturbed system with hamiltonian H_0 , and the interactions between atoms as producing a perturbation H_1 . Thus we have $H = H_0 + H_1$, with

$$H_0 = \sum_i \left\{ \frac{p_i^2}{2M} + \frac{1}{2} M \Omega_0^2 u_i^2 \right\}, \quad (1.1.3)$$

$$H_1 = -\frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} u_i^\alpha u_j^\beta \nabla^\alpha \nabla^\beta V(\mathbf{R}_i - \mathbf{R}_j). \quad (1.1.4)$$

If H is regarded as a classical hamiltonian, the basic theoretical problem is the calculation of the change in the vibration frequency Ω_0 brought about by the interaction H_1 . In quantum-mechanical terms each Einstein oscillator has zero-point energy $\frac{1}{2} \hbar \Omega_0$, and the classical problem can be reformulated as the problem of calculating the change in the zero-point (or ground state) energy of the system. It is convenient for this calculation to consider the more general hamiltonian

$$H(\lambda) = H_0 + \lambda H_1, \quad (1.1.5)$$

where $0 \leq \lambda \leq 1$; this can be interpreted as a gradual "switching on" of the interaction H_1 with parameter λ . The hamiltonian $H(0)$ thus corresponds to the unperturbed problem and $H(1)$ is the full hamiltonian of the original problem. We shall in future drop explicit reference to the superscripts α, β and replace (1.1.4) by

$$H_1 = \frac{1}{2} M \sum_{i \neq j} D_{ij} u_i u_j, \quad \text{with} \quad D_{ij} = D_{ji}. \quad (1.1.6)$$

Thus we ignore the vector character of the displacements \mathbf{u}_i . This is an oversimplification of the original problem which keeps the notation as simple as possible but retains the main features of the formalism.

The exact solution of the classical problem is obtained by writing down the equations of motion of the coupled system and determining the normal modes of vibration. This establishes the propagating modes. From the hamiltonian equations of motion for the hamiltonian $H(\lambda)$ we find that the displacements u_i satisfy the N coupled differential equations

$$\ddot{u}_i + \Omega_0^2 u_i = -\lambda \sum_j D_{ij} u_j. \quad (1.1.7)$$

In fact, because of translational invariance—the fact that every lattice site is equivalent to every other site—these N equations reduce to a single equation. [With the full hamiltonian (1.1.4) we have instead $3N$ coupled equations which can be reduced to 3.]

The mathematical expression of translational invariance is Bloch's theorem, according to which two displacements u_i and u_j differ only by a phase factor:

$$u_j = e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} u_i.$$

In other words, any solution u_i must be of the form

$$u_i(t) = e^{i\mathbf{k} \cdot \mathbf{R}_i} \xi_{\mathbf{k}}(t), \quad (1.1.8)$$

where \mathbf{k} is some wave-vector in the reciprocal lattice. The equation of motion thus reduces to

$$\ddot{\xi}_{\mathbf{k}} + \Omega_0^2 \xi_{\mathbf{k}} = -\lambda \xi_{\mathbf{k}} \sum_j D_{ij} e^{i\mathbf{k} \cdot \mathbf{R}_j}.$$

The sum on the right-hand side must be independent of the origin \mathbf{R}_i , and we write

$$\sum_j D_{ij} e^{i\mathbf{k} \cdot \mathbf{R}_j} = \sum_j D_{ij} e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} = D_{\mathbf{k}} \text{ say,} \quad (1.1.9)$$

where $D_{\mathbf{k}}$ is a Fourier transform of the force function D_{ij} . The inverse formula is

$$D_{ij} = \frac{1}{N} \sum_{\mathbf{k}} D_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}, \quad (1.1.10)$$

where the sum over \mathbf{k} is over all allowed values in the Brillouin zone (determined by periodic boundary conditions). [In the three-dimensional case (assuming one atom per unit cell) of the hamiltonian (1.1.4) $D_{\mathbf{k}}$ becomes a 3×3 matrix $D_{\mathbf{k}}^{\alpha\beta}$, called the *dynamical matrix*.]

Now, for the normal mode of frequency $\Omega_{\mathbf{k}}$, the normal coordinate $\xi_{\mathbf{k}}(t)$ contains a time factor $\exp(i\Omega_{\mathbf{k}}t)$. Putting this into the equation of motion, we immediately obtain our result

$$\Omega_{\mathbf{k}}^2 = \Omega_0^2 + \lambda D_{\mathbf{k}}. \quad (1.1.11)$$

We thus have one normal mode of frequency $\Omega_{\mathbf{k}}$ for each allowed value of \mathbf{k} in the Brillouin zone and, with our choice of (collective) coordinates, the strongly interacting system is reduced to a set of independent simple harmonic oscillators. $\Omega_{\mathbf{k}}$ is the frequency of an *acoustic* mode of vibration. It is easy to prove the relation $\Omega_0^2 + \sum_j D_{ij} = 0$ (this is the

condition that the force on any atom must vanish when all atoms are displaced equally); hence, when $\lambda = 1$, we have $\Omega_{\mathbf{k}} = 0$ at $\mathbf{k} = 0$. The coupling between oscillators represented by the hamiltonian H_1 is thus a *large* perturbation at $\mathbf{k} = 0$, reducing the unperturbed frequency Ω_0 to zero. For small values of $|\mathbf{k}|$ $\Omega_{\mathbf{k}}$ is linear in $|\mathbf{k}|$ and hence represents sound-wave propagation.

When the same problem is formulated in quantum-mechanical terms, the solution is equally simple. The displacements u_i and conjugate momenta p_i are now operators, and the classical hamiltonian can be re-interpreted as the hamiltonian of a set of independent harmonic quantum oscillators. Each simple harmonic oscillation of frequency $\Omega_{\mathbf{k}}$ corresponds to a quantum oscillator whose ground state energy is the zero-point energy $\frac{1}{2}\hbar\Omega_{\mathbf{k}}$. When we wish to emphasize the particle aspect of these quantized acoustic excitations, we speak of *phonons* with which can be associated crystal momentum $\hbar\mathbf{k}$ and energy $\hbar\Omega_{\mathbf{k}}$. The total ground state energy of the lattice is obtained by summing over all modes \mathbf{k} , and the *change* in the ground state energy E_G due to the interaction H_1 is therefore

$$\Delta E_G = \frac{1}{2}\hbar \sum_{\mathbf{k}} (\Omega_{\mathbf{k}} - \Omega_0), \quad (1.1.12)$$

where $\Omega_{\mathbf{k}}$ is given by (1.1.11) with $\lambda = 1$. (We choose units such that $\hbar = 1$ in future.)