We now make an important approximation. We shall see that $F(\mathbf{q}, t)$ describes inelastic scattering in which phonons are emitted or absorbed by the scattered neutron. Usually the one-phonon processes, in which a single phonon is emitted or absorbed, dominate. We shall confine attention to these. This allows us to expand the exponentials in Eq. (1.3.11) and to keep only terms in the matrix element which involve products of two u operators. (The leading term, in which the exponentials are replaced by unity, represents elastic scattering and is of no interest here.) Furthermore, we are only interested in terms which involve u-operators at *different* times (the other terms are time-independent and lead to an overall factor—the "Debye-Waller factor"—multiplying the magnitude of the scattering cross-section. It is also easily seen that the expectation values of *single* u-operators are zero.) The higher-order terms in the expansion of (1.3.11), involving products of more than two u-operators, correspond to multi-phonon processes and will be neglected. Finally, we suppose for simplicity that the polarization of the phonon mode of interest is parallel to $\mathbf{q}$, so that the product $\mathbf{q} \cdot \mathbf{u}_j$ can be replaced by the scalar qu_j.

With all these approximations (and omitting the Debye-Waller factor), the correlation function (1.3.11) reduces to

$$F(\mathbf{q}, t) \simeq q^2 \sum_{jl} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_j)} \langle \psi_G | \tilde{u}_j(t) \tilde{u}_l(0) | \psi_G \rangle, \tag{1.3.12}$$

where $\tilde{u}(t)$ is a Heisenberg operator as in (1.3.8).

1.4. THE GREEN'S FUNCTION AND ITS EQUATION OF MOTION

In Eqs. (1.2.4) and (1.3.12) we now have two examples, one time-independent and the other time-dependent, of correlation functions of interest in the lattice problem. These, and similar correlation functions, are conveniently calculated by means of Green's functions.

First we recall some general quantum-theoretical formulas [see Messiah (1961, Chap. VIII)]. In the Schrödinger picture or "representation" of quantum mechanics the vector $|\Psi_S(t)\rangle$ representing the state of a system at time t evolves in time in accordance with the Schrödinger equation

$$i \frac{\partial |\Psi_S\rangle}{\partial t} = H |\Psi_S\rangle. \tag{1.4.1}$$

This has the formal solution (assuming that H does not depend explicitly on the time)

$$|\Psi_S(t)\rangle = e^{-iH(t-t_0)}|\Psi_S(t_0)\rangle, \tag{1.4.2}$$

which describes the evolution of the system from time t_0 to time t. The physical observables are time-independent operators $\mathcal{O}_S$ in the vector space of the Schrödinger vectors $|\Psi_S\rangle$. The Heisenberg picture or "representation" is an entirely equivalent formulation, obtained from the Schrödinger picture by a unitary transformation to new state vectors $|\Psi_H\rangle$ and observables $\mathcal{O}_H$, defined by

$$|\Psi_H\rangle = e^{iH(t-t_0)}|\Psi_S(t)\rangle = |\Psi_S(t_0)\rangle, \tag{1.4.3}$$

$$\mathcal{O}_H(t) = e^{iH(t-t_0)}\mathcal{O}_S\, e^{-iH(t-t_0)}. \tag{1.4.4}$$

(It is immediately verified that this transformation leaves all matrix elements invariant.) Thus the state vectors are now stationary, and the time dependence has been transferred to the observables. Note that the hamiltonian H is unchanged by the transformation (1.4.4). Instead of the Schrödinger equation we now have the Heisenberg equation of motion which determines the time development of the Heisenberg operators. This is obtained by differentiating (1.4.4):

$$i\frac{d\mathcal{O}_H}{dt} = [\mathcal{O}_H, H], \tag{1.4.5}$$

where the square bracket denotes the commutator $\mathcal{O}_H H - H\mathcal{O}_H$. This is to be solved with the initial condition $\mathcal{O}_H(t_0) = \mathcal{O}_S$.

We now define the single-particle *Green's function* or *propagator* for the phonon problem as

$$G_{ij}(t-t') = -i\langle T[\tilde{u}_i(t)\tilde{u}_j(t')]\rangle_\lambda. \tag{1.4.6}$$

Here the Heisenberg picture is used for operators and state-vectors: thus $\tilde{u}_i(t)$ is a time-dependent operator defined as in Eqs. (1.3.8) or (1.4.4) (with $t_0 = 0$), H being the hamiltonian $H_0 + \lambda H_1$ of the lattice with coupling constant λ, and the expectation value $\langle\cdots\rangle_\lambda$ refers to the exact ground state of the system described by the time-independent Heisenberg vector $|\Psi_G(\lambda)\rangle$ which is assumed to be normalized. The symbol T is Dyson's time-ordering operator which rearranges the product of two time-dependent operators so that the operator which refers to the later time always stands on the left:

$$T[A(t)B(t')] = A(t)B(t') \qquad (t > t')$$
$$= B(t')A(t) \qquad (t < t'). \tag{1.4.7}$$

In the language of second quantization (see Appendix 1) the $\tilde{u}_i$ are field operators, and the Green's function is an expectation value of a product of such operators; as such it is simply (in general) a function of space and time coordinates. In fact, in the present problem the $\tilde{u}_i$ are localized operators containing no space dependence, and G_{ij} is thus a function only of time. Moreover, if H is independent of t, G is a function of the difference $t - t'$ of its arguments, as indicated in Eq. (1.4.6); this follows at once from the analysis of Appendix 2. The presence of the T symbol in the definition of G introduces the discontinuity at $t = t'$ which is characteristic of a Green's function. More generally, if the Green's function is formed from field operators which are expanded in terms of space-dependent basis functions such as plane waves [see Appendix 1, Eq. (A.1.13)], G will be a function of space coordinates $\mathbf{x}$, $\mathbf{x}'$ as well as of t and t'.

G_{ij} as defined in Eq. (1.4.6) is an example of a *time-ordered* or *causal* Green's function. It describes the propagation of disturbances in which a single particle is added to the many-particle equilibrium system at some time instant and removed again at a later time. In the present example G represents the propagation of phonon modes through the crystal lattice. Other Green's functions may de defined, and examples of these will be encountered later: in particular, the *retarded* single-particle Green's function is, for the present problem, given by

$$G_{ij}^{R}(t - t') = -i\theta(t - t')\langle[\tilde{u}_i(t), \tilde{u}_j(t')]\rangle_\lambda, \tag{1.4.8}$$

and the *advanced* Green's function is

$$G_{ij}^{A}(t - t') = i\theta(t' - t)\langle[\tilde{u}_i(t), \tilde{u}_j(t')]\rangle_\lambda, \tag{1.4.9}$$

where $\theta(t)$ is the *unit function* ($\theta(t) = 1$ for $t > 0$, $\theta(t) = 0$ for $t < 0$). Thus, for fixed t', the retarded function exists only for times t later than t', and the advanced function exists only for times t earlier than t'. We shall find when we consider the theory of linear response in later chapters that response functions such as electrical conductivity (Chap. 5), dielectric response (Chap. 6), and magnetic susceptibility (Chap. 7) are obtained in the form of retarded Green's functions. These are directly measurable quantities. Furthermore, retarded and advanced Green's functions have the advantage of possessing particularly simple analytical properties. On the other hand, we shall see in Chap. 3 that the time-ordered functions are particularly well adapted to evaluation by means of diagrammatic perturbation theory. In the present problem, where everything can be calculated exactly, we could use any of these Green's functions for our analysis, and we shall continue to work with the time-ordered form. There are general relations between the different Green's functions, some of which are derived in Appendix 2.

We now see that the expectation value required for the ground state energy (1.2.4) is the limit, as t tends to zero from positive values, of $\langle T[\tilde{u}_i(t)\tilde{u}_j(0)]\rangle_\lambda$, and thus we can express ΔE_G in terms of the Green's function as

$$\Delta E_G = \lim_{t\to 0+} \tfrac{1}{2}iM \sum_{i\neq j} D_{ij} \int_0^1 d\lambda G_{ij}(t). \tag{1.4.10}$$

Furthermore, we see that the time correlation function (1.3.12) required for the neutron scattering cross-section can, for $t > 0$, be expressed in terms of G as

$$F(\mathbf{q}, t) = iq^2 \sum_{jl} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_j)} G_{jl}(t) \tag{1.4.11}$$

(the expression so obtained then holds for all t).

We are now ready to consider the calculation of G_{ij}. Several general methods are available. In this chapter we discuss one of these methods, where we proceed by setting up and solving a differential equation (the "equation of motion") for G. This equation is essentially an inhomogeneous form of the Schrödinger equation. The equation-of-motion approach emphasizes the similarity between G and the Green's functions familiar in classical vibration problems.

Since G depends on $t - t'$ there is no loss of generality in putting $t' = 0$. In differentiating, we must be careful to treat correctly the discontinuity at $t = 0$. We write

$$T[\tilde{u}_i(t)\tilde{u}_j(0)] = \theta(t)\tilde{u}_i(t)\tilde{u}_j(0) + \theta(-t)\tilde{u}_j(0)\tilde{u}_i(t),$$

thus splitting the time-ordered Green's function into the sum of retarded and advanced terms. The derivative $d\theta(t)/dt$ is the delta-function $\delta(t)$, and thus

$$i\frac{dG_{ij}(t)}{dt} = \delta(t)\langle \tilde{u}_i(t)\tilde{u}_j(0) - \tilde{u}_j(0)\tilde{u}_i(t)\rangle + \left\langle T\left[\frac{d\tilde{u}_i(t)}{dt}\,\tilde{u}_j(0)\right]\right\rangle.$$

The first term on the right vanishes, since, at equal times $t = 0$, $[u_i, u_j] = 0$. The time derivative in the second term can be obtained from the Heisenberg equation of motion

$$i\frac{d\tilde{u}_i}{dt} = [\tilde{u}_i, H] = e^{iHt}[u_i, H]\; e^{-iHt}.$$

Using $[p_i, u_j] = -i\delta_{ij}$, this is

$$e^{iHt}[u_i, \sum_j p_j{}^2/2M]\; e^{-iHt} = e^{iHt}(ip_i/M)\; e^{-iHt} = i\tilde{p}_i(t)/M,$$

and thus

$$i\frac{dG_{ij}(t)}{dt} = \frac{1}{M}\langle T[\tilde{p}_i(t)\tilde{u}_j(0)]\rangle; \tag{1.4.12}$$

we see that a new Green's function has appeared on the right. Differentiating again,

$$i\frac{d^2G_{ij}(t)}{dt^2} = \frac{\delta(t)}{M}\langle \tilde{p}_i(t)\tilde{u}_j(0) - \tilde{u}_j(0)\tilde{p}_i(t)\rangle$$

$$+\frac{1}{M}\left\langle T\left[\frac{d\tilde{p}_i(t)}{dt}\,\tilde{u}_j(0)\right]\right\rangle. \tag{1.4.13}$$

The first term on the right is

$$\frac{\delta(t)}{M}\langle [p_i, u_j]\rangle = -\frac{i}{M}\,\delta_{ij}\,\delta(t),$$

and to evaluate the second term we require the commutator

$$[p_i, H] = [p_i, \tfrac{1}{2}M\Omega_0{}^2u_i{}^2 + \tfrac{1}{2}\lambda M \sum_{jk} D_{jk}\,u_ju_k]$$

$$= -iM\Omega_0{}^2u_i - i\lambda M \sum_k D_{ik}\,u_k.$$

Since this involves only terms *linear* in the u_i, we see on substitution in Eq. (1.4.13) that the original Green's function now reappears on the right-hand side, and we obtain the closed set of coupled differential equations

$$\left(-\frac{d^2}{dt^2} - \Omega_0{}^2\right) G_{ij}(t) = \frac{1}{M}\,\delta_{ij}\,\delta(t) + \lambda \sum_k D_{ik} G_{kj}(t). \tag{1.4.14}$$

In more general cases, differentiation of a Green's function will not reproduce the original function on the right-hand side, and instead of a closed set of equations we obtain an infinite chain of equations involving Green's functions of successively higher orders. We then have to approximate at some stage to break off the chain, usually by some sort of "decoupling" procedure in which a high-order Green's function is expressed approximately as a product of Green's functions of lower order. The simple closed result obtained in the present problem depends on the special oscillator form of the hamiltonian.

1.5. THE ITERATION SOLUTION FOR *G*

If we know the solution of the equation of motion (1.4.14) for $\lambda = 0$ (corresponding to the unperturbed hamiltonian), we can obtain the general solution by iteration in powers of λ. For $\lambda = 0$, Eq. (1.4.14) reduces to a differential equation, with a delta-function term representing a unit applied impulse, of a form familiar in elementary discussions of Green's functions. The solution of this is clearly diagonal in the suffices i and j, of the form $G^0(t)\,\delta_{ij}$. The differential equation

$$\left(\frac{d^2}{dt^2} + \Omega_0{}^2\right) G^0(t) = -\frac{1}{M}\,\delta(t) \tag{1.5.1}$$

by itself does not, however, determine $G^0(t)$ completely. It tells us that, in each sub-interval $t < 0$ and $t > 0$, G^0 is some linear combination of the elementary solutions $\exp(\pm i\Omega_0 t)$ of the homogeneous equation. It also follows from Eq. (1.5.1) that G^0 is continuous at $t = 0$ and that its first derivative has a discontinuity there of magnitude $(-1/M)$. The time-ordered, retarded and advanced Green's functions all satisfy Eq. (1.5.1) and have these properties, and the distinction between them comes from initial (and final) conditions at $t = \pm\infty$.