Theoretical aspects of Solid State Physics

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Chapter 1

Introduction

Physics is a qualitative science, and physics is an experimental science. In some rare cases a physical problem may have an exact (or high precision) solution as, for example, in the case of spectrum of Hydrogen atom, or for a value of the fundamental constant $e^2/\hbar c$. Typically, however, it is not so, because of two reasons: first, objects are too complicated in almost all cases and, second, physical laws often have an approximate nature. Therefore, to solve a particular problem, one has, first, to invent a physical model, and then to look for a (mathematically correct, if possible) solution. A special attention has to be devoted to "simplest/minimal" models which may have an exact solution. After that, if the proposed model occurs to be successful enough as, for example, many models in classical mechanics, it passes to mathematical or engineering branches of sciences. Mathematics, on the contrary, is a rigorous science, and essentially it is just a language – a typical sequence of step is "Definitions/Axioms → Statements" (often deducted with small clear steps), then again "Definitions/Axioms → Statements", *etc.* Nevertheless, physics remains a very interesting field, because it deals with objects and phenomena of everyday life.

Methods used in theoretical physics are common in different branches of physics. In the present book, the main attention will be given to methods and applications used in Solid State Physics. The book is organized in the following way: we include

- definitions,
- formulas and theorems (typically without proofs which may be found in references),
- models,
- techniques (i.e., how to use different methods), and
- physical results (if possible, given "by fingers").

As the main "language" of the book we choose the canonical quantization technique. Therefore, a reader has to have a knowledge of some mathematics. This is an activation barrier which, however, *must* be overcome.

1.1 The main ideas

The main ideas are the following.

Hamiltonian. In a general case, Hamiltonian of a system of M nuclei ($M \sim 10^{23}$) and $N = MZ$ electrons ($Z = 3$ to 100 according to the Mendeleev table) has the following form:

$H =$ kinetic energy of nuclei + energy of repulsion of the nuclei − energy of interaction of the positive background with itself	$\to H_{\text{phonons}}$
+ energy of repulsion of electrons − energy of interaction of the negative background with itself	$\to \sum_{q\neq 0}(2\pi e^2/q^2)\left(\rho_q^*\rho_q - n\right)$ (exchange and correlation effects)
+ kinetic energy of electrons	$\to \sum_{k\sigma}(\hbar^2 k^2/2m)\, c^*_{k\sigma}c_{k\sigma}$
+ potential energy of interaction of electrons with nuclei in equilibrium state − energy of interaction of the positive and negative backgrounds	$\to \sum_{kk'\sigma}\left(H_{kk'} - \delta_{kk'}\hbar^2 k^2/2m\right) c^*_{k\sigma}c_{k'\sigma}$
+ potential energy of interaction of electrons with moving nuclei	$\to H_{\text{el-ph}} = \sum_{kqj\sigma} F(qj)\, c^*_{k+q,\sigma}c_{k\sigma}\left(a^*_{qj} + a_{qj}\right)$

Methods of solution. Usually one has to use one or another approximate method, such as the self-consistent field (SCF) method, the Hartree–Fock (HF) approximation, the mean field (MF) method, the random phase approximation (RPA), *etc*. All these methods are in fact different variants of the MF approximation, or the lowest-order approximation of a perturbation theory. Often a hierarchy of characteristic times helps to simplify essentially the solution of the problem (as an example, the adiabatic approximation will be consider in ...).

Probably, the most powerful approach in theoretical physics is to reduce the whole Hamiltonian to one describing a set of weakly-interacting quasi-particles, such as

– phonons (acoustical and optical if the lattice is complex),
– electron-hole pairs (one-electron excitations),
– excitons (in semiconductors),
– plasmons (due to Coulomb interaction between electrons),
– polarons (due to electron-phonon interaction),
– polaritons,
– magnons, *etc.*,

i.e., one has to calculate effective parameters of these quasi-particles as well as their mutual interactions. Thus, a solution may be found approximately only.

Steps. During solution of a problem one typically has to pass through few steps, looking for answers on the following questions:

(A) – how to reduce H to $H_{\text{quasiparticles}}$ (that may be done approximate only),
(B) – what to calculate (e.g., correlation functions and/or response functions),
(C) – how to calculate (e.g., by the Green function technique).

Details of the steps:

(A) – A rigorous reduction of H to $H_{\text{quasiparticles}}$ has no sense; we have to guess the model (i.e. $H_{\text{quasiparticles}}$) from the very beginning (the main requirement here is that the model must be maximally simple, but it should correctly describe the object or phenomenon under interest), and then only (sometimes much later) the introduced model may find a background (examples will be given below in the book).

(B) – What to calculate? If we are interesting in *the equilibrium state* of the system, then the distribution function

$$\rho(\ldots) \propto \exp -\beta H(\ldots) \tag{1.1}$$

should be calculated. For calculation of thermodynamic potentials, we need to know the one-particle distribution function $\rho(x)$ and the two-particle function $\rho(x_1, x_2)$, i.e. the general function (1.1) should be integrated over all coordinates except x_1 and x_2.

In a general *nonequilibrium* case, the correlation function

$$Q_{AB}(t_1, t_2) = \langle \delta A(t_1)\, \delta B(t_2) \rangle \tag{1.2}$$

should be known. It contains almost all information about the system. Namely, at experiment one could measure:

(a) the scattering cross-section

$$\frac{\partial^2 \sigma}{\partial \Omega\, \partial \varepsilon} \propto \widehat{Q}_{AB}(\omega, k)\,. \tag{1.3}$$

In elastic scattering experiments (= diffraction) one measures the structure factor. In inelastic scattering experiments, we obtain the spectrum of system excitations. In both cases, the so-called Debye-Waller (DW) factor may be measured (see below).

(b) the response function (if a perturbation of the system because of measuring may be considered as a "small" one)

$$\langle \delta A \rangle \propto \int \ldots \alpha(\ldots)\, F(\ldots)\,, \tag{1.4}$$

where α is the generalized susceptibility; the latter is coupled with $\widehat{Q}$ by the fluctuation-dissipation theorem (FDT, or the famous Niquist theorem).

(C) – How to calculate? In particular, one of useful methods is the Green function technique. Its idea is the following: let we need to solve the problem

$$A\phi = b. \tag{1.5}$$

Let us first solve the problem

$$AG = 1, \quad \text{or} \quad G = A^{-1}, \tag{1.6}$$

then the solution for a general case is given by

$$\phi = Gb\,. \tag{1.7}$$

An advantage of this approach is that Eq. (1.6) has to be solved once only; then we have the solution for any b (examples will be given below).

Chapter 2

Mathematical Introduction

2.1 Hilbert Space

The laws of quantum mechanics are formulated in the so-called *Hilbert space.* Namely, a state of a quantum-mechanical system is described by a *vector* (element) of the Hilbert space, and any change of the state (e.g., measure of some quantity, or system evolution, *etc.*) is described by action of a corresponding *operator* defined in the Hilbert space. Below we give in brief the main definitions.

Space is a set of elements called *vectors.* A vector is denoted by ψ or $|\psi\rangle$.

Topological space is ... A special case of topological space is the metric space. *Metric space* is the space where a metrics $\rho(\psi_1, \psi_2)$ is defined for any two elements.

Linear space is the space where the following two operations are defined: (1) the *sum* operation, i.e. a rule which puts into correspondence a vector $|\psi_3\rangle = |\psi_1\rangle + |\psi_2\rangle$, belonging to the same space, for any two vectors $|\psi_1\rangle$ and $|\psi_2\rangle$. The sum operation is commutative; (2) the operation of *multiplying on a complex number*, i.e., if c is a complex number, the vector $|\psi_2\rangle = c|\psi_1\rangle$ should belong to the same space. These two operations must also satisfy the two rules $(\alpha + \beta)|\psi\rangle = \alpha|\psi\rangle + \beta|\psi\rangle$ and $\alpha(|\psi_1\rangle + |\psi_2\rangle) = \alpha|\psi_1\rangle + \alpha|\psi_2\rangle$.

Normalized space is the linear space where every element has its own *norm* denoted $\|\psi\|$. The norm of an element is a number, associated with this element, which must satisfy the following three conditions:
(1) $\|\psi\| \geq 0$, and $\|\psi\| = 0$ if and only if $\psi = 0$;
(2) $\|\psi_1 + \psi_2\| \leq \|\psi_1\| + \|\psi_2\|$;
(3) $\|\alpha\psi\| = |\alpha| \cdot \|\psi\|$.

Complete space is the normalized space where any fundamental sequence of elements (i.e. a sequence that satisfies the Cauchy condition) converges to an element belonging to the same space. If the space is not complete, it may be completed by adding the corresponding converging elements.

The linear normalized complete space is called the *Banach space.*

Basis is a special set of vectors of the complete space such that any other vector may be presented as a linear combination of the basic elements.

Separable space is the complete space which has a countable everywhere-dense subset. The basis of the separable space consists of countable number of vectors.

Euclidean space is the (linear) complete space where a *scalar product* is defined, i.e., a complex number $c = \langle\psi_1|\psi_2\rangle$ is associated with any two vectors $|\psi_1\rangle$ and $|\psi_2\rangle$. The scalar product must satisfy the following three conditions:

(1) linearity,

(2) symmetry, $\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle$, and

(3) $\langle\psi|\psi\rangle \geq 0$, and $\langle\psi|\psi\rangle = 0$ if and only if $\psi = 0$.

Two (nonzero) elements are called *ortogonal* if $\langle\psi_1|\psi_2\rangle = 0$.

Comment 1: The norm in the Euclidean space is defined as $\|\psi\| = \sqrt{\langle\psi|\psi\rangle}$. The CB inequality, $|\langle\psi_1|\psi_2\rangle| \leq \|\psi_1\| \cdot \|\psi_2\|$, is always valid in the Euclidean space.

Comment 2: In the normalized space, if the norm satisfies the condition

$$\|\psi_1 + \psi_2\|^2 + \|\psi_1 - \psi_2\|^2 = 2\left(\|\psi_1\|^2 + \|\psi_2\|^2\right),$$

then the scalar product may be defined as

$$\langle\psi_1|\psi_2\rangle = \frac{1}{4}\left(\|\psi_1 + \psi_2\|^2 - \|\psi_1 - \psi_2\|^2\right).$$

Theorem: The Euclidean space always has the orthonormal basis (i.e. the basis which is countable and complete, and its vectors are normalized and orthogonal). The presentation of a vector over this basis is called the (generalized) *Fourier series*.

Hilbert space is the (complete) separable Euclidean space. Its basis may be finite or infinite (rigorously, the basis must be infinite, but in quantum mechanics the basis is often finite, so we will not use this restriction). All infinite Hilbert spaces are isomorphic each other.

Operator A is an operation which, acting on a vector, produces (another) vector belonging to the same space, $|\psi_2\rangle = A|\psi_1\rangle$.

The simplest operator is the identity operator $\mathbf{1}$ which does not change the vector under action. If $\{\varphi_i\}$ is the basis of the Hilbert space, then

$$\mathbf{1} = \sum_i^{\text{all}} |\varphi_i\rangle\langle\varphi_i|\,. \tag{2.1}$$

Hermitian conjugate A^* of an operator A is defined by the equation

$$\langle\psi_1|A\psi_2\rangle = \langle\psi_1 A^*|\psi_2\rangle\,. \tag{2.2}$$

Note: $(\ldots ABC\ldots)^* = \ldots C^*B^*A^*\ldots$

Inverse operator A^{-1} is defined by the equation

$$A^{-1}A = \mathbf{1}. \tag{2.3}$$

Operator A is called *Hermitian* if $A^* = A$.

Operator U is called *unitary* if $U^{-1} = U^*$.

2.2 The main postulates of quantum mechanics

1. *Any state* of a system is described by a *vector in a Hilbert space* corresponded to the given system.

2. *Any measurable quantity* of the system is described by a corresponding *linear Hermitian operator* called *observable* which acts in this space.

3. *Any symmetry* of the system is described by a corresponding *unitary operator*.

2.3 Bases

2.3.1 Discrete basis: a general case

Let A is a observable, and

$$A|a_i\rangle = a_i|a_i\rangle. \tag{2.4}$$

Then $|a_i\rangle$ are known as eigenvectors and a_i as eigenvalues, $i = 1, 2, \ldots, n$ (may be $n = \infty$).

Condition of *completeness* of the set of eigenvector is

$$\sum_i |a_i\rangle\langle a_i| = \mathbf{1}. \tag{2.5}$$

Ortonormality condition takes the form

$$\langle a_i|a_k\rangle = \delta_{ik}. \tag{2.6}$$

The complete orthonormal basis is the best one. However, non-orthogonal and unnormalized bases may be used as well – sometimes they may lead to a more clear physical picture, although algebra becomes more lengthy. In studying complex quantum-mechanical systems the basis is often incomplete; this results in an approximate description of the system. Emphasize that the basis *should not be overcomplete*, because this could lead to artifacts.

2.3.2 Space $\mathbf{L}_2(X)$

The space $L_2(X)$ is the set $\{f(x)\}$ of all real functions defined on the interval X, such that (1) all functions are integrable according to Lebesgue measure $\mu(X) < \infty$, and (2) for any function, $\int dx\, f^2(x) < \infty$.

The space $L_2(X)$ is the Hilbert space. The scalar product in this space is defined as

$$\langle\psi_1|\psi_2\rangle = \int dx\, \psi_1(x)\, \psi_2(x)\,. \tag{2.7}$$

The following bases may be introduced in this space:

1. For the finite interval $(0, \pi)$ the functions $\{\sin(kx),\ \cos(kx)\}$, where $k = 0, 1, \ldots, \infty$, constitute the basis. Any function may be expanded over this basis, and this expansion is known as the conventional Fourier series.

2. For the finite interval $(0, 1)$ the set of functions $\{x^k\}$, where $k = 0, 1, \ldots, \infty$, constitutes the basis. Any function may be expanded over this basis, the expansion is known as the Taylor series. This basis is not orthogonal, but it may be orthogonalized; the resulting polynomials are called the Legendre polynomials.

3. The set of functions $\{x^k e^{-x^2}\}$ constitutes the basis on the $(-\infty, \infty)$ interval. Being orthonormalized, these functions are known as the Chebyshev–Hermite polynomials.

4. The set of functions $\{x^k e^{-x}\}$ constitutes the basis on the $(0, \infty)$ interval. Being orthonormalized, these functions are called the Laguerre polynomials.

2.3.3 Continuous Basis

The set of points of the interval $(-\infty, \infty)$ is uncountable, so the corresponding space is not Hilbert. Being overcomplete, it may lead to artifacts when used as the vector space in quantum mechanics. However, due to its convenience, it is often used as the space in some quantum-mechanical problems such as, e.g., the scattering problem. This basis is defined by

$$Q|q\rangle = q|q\rangle\,. \tag{2.8}$$

The condition of *completeness* of the eigenvector set is

$$\int |q\rangle\, dq\, \langle q| = \mathbf{1}. \tag{2.9}$$

Ortonormality in the continuous basis takes the form

$$\langle q'|q''\rangle = \delta(q' - q'')\,. \tag{2.10}$$

The *wave function* for the state $|p\rangle$ is introduced as

$$\psi_p(q) = \langle q|p\rangle\,. \tag{2.11}$$

The *scalar product* is defined by the integral

$$\langle r|p\rangle = \int \langle r|q'\rangle\, dq'\, \langle q'|p\rangle = \int dq'\, \psi_r^*(q')\psi_p(q')\,. \tag{2.12}$$

The action of an *operator* is described by the integral

$$\langle r|f(Q)|p\rangle = \int \langle r|q'\rangle\, dq'\, \langle q'|p\rangle = \int dq''\, \psi_r^*(q'')f(q'')\psi_p(q'')\,. \tag{2.13}$$

Example: the momentum operator $P = -i\frac{\partial}{\partial Q}$ acts by

$$\langle q''|P|q'\rangle = -i\frac{\partial}{\partial q'}\,\delta(q' - q'')\,, \tag{2.14}$$

so that

$$\langle r|P|p\rangle = \int dq''\, \psi_r^*(q'')\left[-i\frac{\partial}{\partial q''}\psi_p(q'')\right]. \tag{2.15}$$

2.4 Basis for canonical quantization

Canonical (second, secondary) quantization is neither "second" nor "quantization". The canonical quantization is simply a very useful language in description of a system of $N \geq 2$ identical particles, especially when the number of particles is not conserved.

The canonical quantization Hilbert space L_N for the system of N *identical* particles is constructed with the help of the Hilbert space L_1 of a single particle. Namely, if $\{\varphi_i\}$ is the basis of the space L_1, a vector of the space L_N is denoted as

$$|n_{i_1}, n_{i_2}, n_{i_3}, \ldots\rangle\,. \tag{2.16}$$

This vector describes the system state where there are n_{i_1} particles in the state φ_{i_1}, n_{i_2} particles in the state φ_{i_2}, *etc.* Therefore, L_N is also called the *space of occupation numbers*. Any vector of this space may be transformed into another vector by action of a combination of the so-called *creation* and *annihilation* operators, so any operator may be expressed through these special operators. Moreover, any state of L_N for any N may be constructed with the help of creation operators from a single vector

$$|0\rangle \equiv |0_{i_1}, 0_{i_2}, 0_{i_3}, \ldots\rangle\,, \tag{2.17}$$

which is called *the vacuum state*.

Let us describe this construction in detail. The Hilbert space for the system of $N \geq 2$ identical particles may be constructed from the $N = 1$ space in the following way: Let we already constructed the Hilbert space $L_1 \equiv \{\varphi_i\}$ for the system of *one* particle. Then, for the system of *two* particles it seems natural to choose, as the Hilbert space, the direct product of two copies of the one-particle Hilbert space, $L_2 = L_1 \bigotimes L_1 \equiv \{\varphi_{ij}^{(2)} = \varphi_i \varphi_j\}$. When these two particles are not identical, this construction is correct. However, for the system of *identical* particles it is not so, the space L_2 is overcomplete. Indeed, the vectors $|i, j\rangle$ and $|j, i\rangle$ are *different* vectors of L_2, but both vectors describe the *same* state of the quantum-mechanical system, because the identical particles cannot be distinguished, and the permutation of two particles must not change the system state. Therefore, this uncertainty must be excluded, extra vectors should be removed from the Hilbert space. On the other hand, according to the axiom 5 of quantum mechanics (see below Sec. 3.1), the vectors φ and $e^{i\alpha}\varphi$ with α being real, describe the same state of the quantum-mechanical system, and a freedom in choosing of α leads to different constructions of the Hilbert space, which correspond to different types of particles (in nature, however, only two types of particles are realized, the Bose particles and the Fermi particles).

The "canonical quantization" method of construction of the Hilbert space for the system of $N \geq 2$ identical particles consists of the following six simple steps:
(1) *Choose* a basis $\{\varphi_i\} \equiv \{|i\rangle\}$ for the one-particle ($N = 1$) system.
(2) Formally introduce the state $|0\rangle$ called the *vacuum state*. For a physical system this state corresponds to the state without particles ($N = 0$).
(3) *Define the creation operator* c_i^* by the equation

$$|i\rangle = c_i^* |0\rangle. \tag{2.18}$$

(4) *Define the annihilation operator* c_i as the Hermitian conjugate of the creation operator, $c_i = (c_i^*)^*$, and *define* the vacuum state by the equation

$$c_i |0\rangle = 0. \tag{2.19}$$

Equation (2.19) is physically clear: it is nothing to destroy in the vacuum state, where there are no particles.
(5) *Choose* permutation relations for the operators introduced above (either commutate or anticommutate rules, see below).
(6) Finally, a state of the system consisting of N particles is obtained by the consequent (N-times) action of creation operators on the vacuum state.

Let us describe these steps in more details and show that they are self-consistent and rigorous.

The step **(1)** has been already described above.

The step **(2)** is formal and, therefore, needs no explanation.

Let us show that the definitions **(3)** and **(4)** are self-consistent: the action of the annihilation operator c_i, defined as the Hermitian conjugate of the operator c_i^*, on the state $|i\rangle$ produces the vacuum state, $c_i|i\rangle = |0\rangle$. Indeed, multiplying both sides of Eq. (2.19) on $\langle 0|$ from the left-hand-side (l.h.s.), we obtain the identity:

$$\langle 0|c_i|i\rangle = (\langle i|c_i^*|0\rangle)^* = (\langle i|i\rangle)^* = 1 = \langle 0|0\rangle = 1. \tag{2.20}$$

The step **(5)** defines the rules for consequent action of creation and annihilation operators. Namely, the state with two particles, one in the state $|i\rangle$ and another in the state $|j\rangle$ ($j \neq i$), may be created in two ways: as $|\varphi_1^{(2)}\rangle = c_i^* c_j^* |0\rangle$ or as $|\varphi_2^{(2)}\rangle = c_j^* c_i^* |0\rangle$. Because both vectors describe the same state, they must be coupled by the relation $|\varphi_1^{(2)}\rangle = e^{i\alpha}|\varphi_2^{(2)}\rangle$. Different choices of the real α result in different Hilbert spaces. In quantum mechanics, only two choices are used: $\alpha = 0$ and $\alpha = \pi$, or $|\varphi_1^{(2)}\rangle = \pm|\varphi_2^{(2)}\rangle$. Thus, we have to take

$$c_i^* c_j^* = \pm c_j^* c_i^* . \tag{2.21}$$

The plus sign describes Bose particles, and the minus sign corresponds to Fermi particles. For the Fermi case we automatically obtain from (2.21) that $c_i^* c_i^* = 0$, i.e. the configuration with two particles in the same state is forbidden. This is the well-known *Pauli principle*.

To find the commutator for c_i and c_i^*, let us use the fact that the basis $\{\varphi_i\}$ is orthonormal, $\langle j|i\rangle = \delta_{ij}$. Because $|i\rangle = c_i^*|0\rangle$ and $|j\rangle = c_j^*|0\rangle$, or $\langle j| = \langle 0|c_j$, we obtain $\langle j|i\rangle = \langle 0|c_j c_i^*|0\rangle = \delta_{ij}$. Using the definition of the vacuum state, this equation may be rewritten as $\langle 0|c_j c_i^* \mp c_i^* c_j|0\rangle = \langle 0|\delta_{ij}|0\rangle$. The later may be satisfied, if we assume that

$$c_j c_i^* \mp c_i^* c_j \equiv [c_j c_i^*]_{-\eta} = \delta_{ij} \,. \tag{2.22}$$

One can easily check that Eq. (2.22) is consistent with all other definitions introduced above.

As was shown above, for the Fermi particles the same state cannot be occupied by two particles. Now let us calculate the probability that the same state is occupied by two Bose particles, i.e. let us calculate $|\varphi^{(2)}|^2$ for the vector $\varphi^{(2)} = c^* c^*|0\rangle$. Using the Bose commutation rule, we obtain

$$\begin{aligned}\langle\varphi^{(2)}|\varphi^{(2)}\rangle &= \langle 0|cc c^* c^*|0\rangle = \langle 0|c(1 + c^* c)c^*|0\rangle = \langle 0|cc^*|0\rangle + \langle 0|cc^* cc^*|0\rangle \\ &= 1 + \langle 0|cc^*(1 + c^* c)|0\rangle = 1 + 1 = 2.\end{aligned} \tag{2.23}$$

Analogously one can obtain that $|\varphi^{(N)}|^2 = N!$ for the vector $\varphi^{(N)} = (c^*)^N|0\rangle$. This is the well-known *Bose condensation*: Bose particles prefer to occupy the same state; at $T = 0$ this clearly should be the state with the lowest energy.

Let us summarize all rules together separately for Bose and Fermi particles.

2.4.1 Bose particles

Commutators:

$$[c, c^*]_- = 1, \quad \text{all others} = 0. \tag{2.24}$$

Normalized basic vectors, $\langle n|n\rangle = 1$, are defined by

$$|n\rangle = \frac{1}{\sqrt{n!}}\,(c^*)^n\,|0\rangle. \tag{2.25}$$

Action of creation and annihilation operators on the basic vectors is described by the following relations:

$$\begin{array}{ll} c^*\,|0\rangle = |1\rangle, & c\,|0\rangle = 0, \\ c^*|1\rangle = \sqrt{2}\,|2\rangle, & c\,|1\rangle = |0\rangle, \\ c^*|2\rangle = \sqrt{3}\,|3\rangle, & c\,|2\rangle = \sqrt{2}\,|1\rangle, \\ \ldots & \ldots \\ c^*|n\rangle = \sqrt{n+1}\,|n+1\rangle, & c\,|n\rangle = \sqrt{n}\,|n-1\rangle. \end{array} \tag{2.26}$$

2.4.2 Fermi particles

Commutators:

$$[c_i, c_j^*]_+ = \delta_{ij}, \quad \text{all others} = 0. \tag{2.27}$$

Action of creation and annihilation operators on the basic vectors is:

$$c_j|\dots, 0_j, \dots\rangle = 0, \tag{2.28}$$

$$c_j^*|\dots, 0_j, \dots\rangle = (-1)^{p_j}|\dots, 1_j, \dots\rangle, \tag{2.29}$$

$$c_j|\dots, 1_j, \dots\rangle = (-1)^{p_j}|\dots, 0_j, \dots\rangle, \tag{2.30}$$

$$c_j^*|\dots, 1_j, \dots\rangle = 0, \tag{2.31}$$

where p_j is the total number of *occupied* states which are to the left of the state j.

2.5 Analytical Functions

A complex function $f(z)$ is defined as a rule which puts in a correspondence one point z of the complex plane to another point $w \equiv f(z)$,

$$z = x + iy \quad \to \quad w = u + iv. \tag{2.32}$$

Regular (*analytical*) function $f(z)$ at a *given* point $z = \xi$ is defined as the function which has the so-called Laurent's series near this point, i.e. if it can be presented as the series

$$f(z) = \sum_{n=0}^{\infty} c_n \, (z - \xi)^n, \tag{2.33}$$

which converges within a circle $|z - \xi| < r$ with $r > 0$. The function is regular if and only if it is differentiable, i.e.

$$\text{...} \tag{2.34}$$

The coefficients in the Laurent series can be found by the integrands

$$c_n = \frac{1}{2\pi i} \int dz \, \frac{f(z)}{(z - \xi)^{n+1}} \,. \tag{2.35}$$

The regular function is differentiable an infinite number of times, and

$$f^{(n)}(z) = \frac{n!}{2\pi i} \int d\xi \, \frac{f(\xi)}{(\xi - z)^{n+1}} \,. \tag{2.36}$$

Analytical continuation: Let $f_\alpha(z)$ is a regular function at a point $z = \alpha$, and let Γ is a curve which begins at the point $z = \alpha$. Then the doublet $\{z, \Gamma\}$, where Γ connects a point z with the initial point α, defines the *Riemann surface.* The function $f(z)$ is called the analytical continuation of $f_\alpha(z)$ on the curve Γ, if $f(z)$ is regular for any point $z \in \Gamma$ (Note: such a procedure is dined if there is a special point, see below). Then, we may define in a similar way the function which is analytical (regular) in a simply connected domain $\mathcal{G}$: *Analytic function in a domain* is the function which is analytical at any point within this domain.

Cauchy: if $f(z)$ is regular in $\mathcal{G}$, $\mathcal{G}$ is a finite simply connected domain, and $C \in \mathcal{G}$ is a closed simple curve, then

$$\oint_C dz \, f(z) = 0 \tag{2.37}$$

and

$$f(z)=\frac{1}{2\pi i}\oint_C d\xi\,\frac{f(\xi)}{\xi-z}\,. \tag{2.38}$$

If a function cannot be analytically continued to a point ξ, this point is called the *special point*. A special point is called the *isolated special point*, if the function is regular within the ring $0<|z-\xi|<R$. An isolated special point is called the *pole*, if $1/f(z)$ has the k-order zero (otherwise the isolated special point is called the *essentially special point*). For poles, the residue theory operates.

2.5.1 Fourier and Laplace Transforms

Many properties of Green functions and susceptibility simply follow from analytical properties of functions of a complex variable. Let us summarize here the main definitions and theorems. In what follows, $\omega=\omega_R+i\omega_I$ denotes the complex plane.

A general case

Let $G(t)$ be a function of a *real* variable t, $-\infty<t<+\infty$, and let $|G(t)|<\infty$.
Define the Fourier transform as

$$\widehat{G}(\omega_R)=\int_{-\infty}^{+\infty}dt\;e^{i\omega_R t}G(t)\,. \tag{2.39}$$

Define the Laplace transform as

$$\bar{G}(\omega)=\int_0^{\infty}dt\;e^{i\omega t}G(t)\,,\quad \omega_I>0. \tag{2.40}$$

Define the generalized Laplace transform as

$$\bar{G}(\omega)=\int_{-\infty}^{+\infty}\frac{d\omega_R}{2\pi i}\,\frac{\widehat{G}(\omega_R)}{\omega_R-\omega}\,,\quad \omega_I\neq 0. \tag{2.41}$$

The function (2.41) is analytical everywhere on the ω-plane with the cut along the *real axis*. From (2.41) it follows that

$$\bar{G}(\omega_R\pm i0)=\frac{1}{2\pi i}\,\mathcal{P}\int_{-\infty}^{+\infty}d\omega_R'\,\frac{\widehat{G}(\omega_R')}{\omega_R'-\omega_R}\;\pm\frac{1}{2}\widehat{G}(\omega_R) \tag{2.42}$$

and, therefore,

$$\widehat{G}(\omega_R)=\bar{G}(\omega_R+i0)-\bar{G}(\omega_R-i0)\,. \tag{2.43}$$

The *Wiener-Khintchine theorem* states that

$$\int_{-\infty}^{+\infty}dt\;G_1^*(t)\,G_2(t)=\int_{-\infty}^{+\infty}\frac{d\omega_R}{2\pi}\,\widehat{G}_1^*(\omega_R)\,\widehat{G}_2(\omega_R)\,. \tag{2.44}$$

Note also that if $G(t)$ is an even function, $G(t)=G(-t)$, then

$$\widehat{G}(\omega_R)=\bar{G}(\omega_R+i0)+\bar{G}(-\omega_R+i0)\,. \tag{2.45}$$

A real function

If $G(t)$ is the *real function*, then directly from the definition (2.39) it follows that

$$\widehat{G}^*(\omega_R) = \widehat{G}(-\omega_R)\,, \tag{2.46}$$

i.e. $\mathrm{Re}\,\widehat{G}(\omega_R)$ is the even function, and $\mathrm{Im}\,\widehat{G}(\omega_R)$ is the odd function of ω_R. From Eq. (2.41) we obtain in this case that

$$\bar{G}^*(\omega) = \bar{G}(-\omega^*) \tag{2.47}$$

and, therefore, $\bar{G}(i\omega_I)$ is real.
Connection: calculating $\int_O d\omega\, \omega\, \bar{G}(\omega)\, \left(\omega^2 + \omega_R^2\right)^{-1}$ by two methods, we obtain

$$\int_{-\infty}^{+\infty} d\omega_R' \, \frac{\omega_R'\, \bar{G}(\omega_R' + i0)}{(\omega_R')^2 + \omega_R^2} = i\pi \bar{G}(i\omega_R)\,. \tag{2.48}$$

Note that if $G(t)$ is the even function, then from Eqs. (2.45) and (2.47) it follows that $\widehat{G}(\omega_R)$ is real, and from Eq. (2.42) we obtain

$$\mathrm{Re}\,\bar{G}(\omega_R \pm i0) = \pm\frac{1}{2}\widehat{G}(\omega_R)\,. \tag{2.49}$$

Causality

If $G(t) = 0$ for $t < 0$ (the fundamental concept of causality which describes the relationship between causes and effects), then its Fourier and Laplace transforms have some important properties.

Let us define the function $\widetilde{G}(\omega)$ for all ω in such a way that $\widetilde{G}(\omega) = \bar{G}(\omega)$ for $\omega_I > 0$, while for $\omega_I \le 0$ the function $\widetilde{G}(\omega)$ is defined as analytical continuation of this function. Then the function $\widetilde{G}(\omega)$ is analytical for $\omega_I \ge 0$ and may have special points at $\omega_I < 0$. Moreover, directly from the causality it follows that

$$\widetilde{G}(\omega_R) = \widehat{G}(\omega_R)\,. \tag{2.50}$$

Using Eqs. (2.50) and (2.42), we obtain

$$\widehat{G}(\omega_R) = \frac{1}{\pi i}\ \mathcal{P}\int_{-\infty}^{+\infty} d\omega_R' \, \frac{\widehat{G}(\omega_R')}{\omega_R' - \omega_R}\ . \tag{2.51}$$

Taking the real and imaginary parts of Eq. (2.51), we get

$$\mathrm{Re}\,\widehat{G}(\omega_R) = +\frac{1}{\pi}\ \mathcal{P}\int_{-\infty}^{+\infty} d\omega_R' \, \frac{\mathrm{Im}\,\widehat{G}(\omega_R')}{\omega_R' - \omega_R} \tag{2.52}$$

and

$$\mathrm{Im}\,\widehat{G}(\omega_R) = -\frac{1}{\pi}\ \mathcal{P}\int_{-\infty}^{+\infty} d\omega_R' \, \frac{\mathrm{Re}\,\widehat{G}(\omega_R')}{\omega_R' - \omega_R}\ . \tag{2.53}$$

Then, with (2.52) we get

$$\bar{G}(\omega) = \int_{-\infty}^{+\infty} \frac{d\omega_R}{\pi}\, \frac{\mathrm{Im}\,\widehat{G}(\omega_R)}{\omega_R - \omega} \tag{2.54}$$

(the Kramers–Kronig relation).
Note: it $G(t)$ is real, then from (2.48), (**??**), (**??**) and (**??**) it follows that

$$\bar{G}(i\omega_I) = \frac{2}{\pi}\int_0^{\infty} d\omega_R' \, \frac{\omega_R'\, \mathrm{Im}\,\widehat{G}(\omega_R')}{(\omega_R')^2 + \omega_I^2}\ . \tag{2.55}$$

Integrating $\bar{G}(i\omega_I)$, we obtain

$$\int_0^\infty d\omega_I \, \bar{G}(i\omega_I) = \int_0^\infty d\omega_R \, \mathrm{Im}\, \widehat{G}(\omega_R) \, . \tag{2.56}$$

2.6 Green Functions

The Green function technique is a powerful method which provides the general solution of a problem. This technique is used in different areas and, therefore, may be realized in different ways.

Recall the main idea: if we need to solve the equation $A\phi = b$, we firstly have to find a solution of the problem $G = A^{-1}$, and then the solution for a general case has the form $\phi = Gb$.

Consider the following simple examples (for quantum-mechanical many-particle systems the technique is more involved and will be described in Sec. 6).

2.6.1 Mathematical physics: Diffusion equation

Consider the diffusion (parabolic) equation

$$\dot{u}(x,t) = D\Delta u(x,t) + f(x,t) \, , \tag{2.57}$$

where $f(x,t)$ is called the source, with the initial condition

$$u(x,0) = \varphi(x). \tag{2.58}$$

First let us solve the equation

$$\dot{G} = D \, \Delta G \tag{2.59}$$

with the initial condition

$$G(x,0) = \delta(x). \tag{2.60}$$

The solution of Eq. (2.59) is

$$G(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{x^2}{4Dt} \right) . \tag{2.61}$$

The function (2.61) is the Green function for the problem (2.57). The general solution of Eq. (2.57) can then be expressed as

$$u(x,t) = \int dx' \, \varphi(x') \, G(x-x',t) + \int dx' \int^t dt' \, f(x',t') \, G(x-x',t-t') \, . \tag{2.62}$$

2.6.2 Operator Green function (one-particle problem)

A formal solution of the equation

$$(\omega - H) \, \widehat{G}(\omega) = 1 \tag{2.63}$$

is

$$\widehat{G}^{\pm}(\omega) = (\omega - H \pm i\delta)^{-1}, \quad \delta \to 0. \tag{2.64}$$

If

$$H|n\rangle = E_n |n\rangle, \tag{2.65}$$

then

$$\widehat{G}^{\pm}(\omega)=\sum_n \frac{|n\rangle\langle n|}{\omega-E_n\pm i\delta}\,. \tag{2.66}$$

Thus, the poles of the Green function give the eigen-energies E_n, while residues at these poles give the corresponding eigenfunctions $|n\rangle$.

Then, the density of states is equal to

$$\mathcal{N}(\omega)=\pm\frac{1}{\pi}\,\mathrm{Im}\;\mathrm{Sp}\;\widehat{G}^{\mp}(\omega)\,. \tag{2.67}$$

The main advantage of this technique is proved in the perturbation theory approach. Namely, if

$$H=H_0+V, \tag{2.68}$$

then

$$G=G_0+G_0VG=G_0+GVG_0\,. \tag{2.69}$$

This equation may then be iterated resulting in the perturbation theory series.

2.6.3 Perturbation theory in continuous spectrum

Let

$$H_0\varphi_0=E\varphi_0 \tag{2.70}$$

and

$$(H_0+V)\,\varphi=E\varphi\,. \tag{2.71}$$

Note that here E is the same in both equations! (for a discrete spectrum, the situation is more complicated and inconvenient because of corrections like $E_n^{(0)}\to E_n$).

Equations (2.70, 2.71) may be rewritten as

$$(H_0-E)(\varphi-\varphi_0)=-V\varphi\,. \tag{2.72}$$

Introducing the Green function $G_0=(E-H_0)^{-1}$, the solution may be written as

$$\varphi=\varphi_0+G_0V\varphi \tag{2.73}$$

or, in full notation, as

$$\varphi(x)=\varphi_0(x)+\int dx'\;G_0(x,x';E)\,V(x')\varphi(x')\,. \tag{2.74}$$

In the scattering problem, $\varphi_0(x)$ corresponds to the incoming wave, and one has to use the Green function G_0^+.

2.6.4 Scattering theory

The *scattering operator* is defined as

$$\widehat{T}(\omega)=\widehat{V}+\widehat{V}\,\widehat{G}^0(\omega)\,\widehat{T}(\omega)\,. \tag{2.75}$$

Therefore, we have

$$\begin{aligned} T&=V+VGV\,,\\ TG^0&=VG\,,\\ G^0T&=GV\,,\\ G&=G^0+G^0TG^0\,. \end{aligned} \tag{2.76}$$

Chapter 3

Quantum Mechanics

3.1 Axioms

Any state of a physical system is described by a vector of a corresponding Hilbert space. Laws of the quantum mechanics reduce to the following axioms:

(1) Linear Hermitian operators (called *observable*) **(1)** are used for presentation of measured values.

(2) Eigenvalues of observable operators **(2)** present possible results of the measuring.

(3) If two operators A and B commute, **(3)** then the simultaneous measure of A and B is possible.

(4) Let $[A, B] = 0$, $\psi^{(j)}$ be the eigenvectors of A, and $\varphi^{(k)}$ be the eigenvectors of B. Then two observable operators A and B may be united into a single observable $C = A \bigotimes B$, where the operator C acts in the space $\{\psi^{(j)}\} \bigotimes \{\varphi^{(k)}\}$.

(5) A *normalized* vector ψ **(5)** describes a state of the system.

Note: the same state may be described by the vector $\psi e^{i\beta}$ provided β is a real number.

(6) The projection of ψ onto an eigenvector $\psi^{(j)}$ of the observable A, $p^{(j)}|\psi\rangle = |\psi^{(j)}\rangle\langle\psi^{(j)}|\psi\rangle = c_j\,|\psi^{(j)}\rangle$, **(6)** characterizes the possibility to obtain at measuring the value $a^{(j)}$.

(7) The *probability* to obtain the value $a^{(j)}$ is equal to $c_j^* c_j$.

(8) The *average value* of the observable A for the system in the state ψ is equal to $\overline{A} = \langle\psi|A\psi\rangle = \sum_j (c_j^* c_j)\, a^{(j)}$. $\overline{A}$ is real, because A is Hermitian.

(9) If $\varphi = B\,\psi$, then $\overline{B} = \langle\psi|\varphi\rangle = \psi^*\varphi$. The probability of the transition of the system from the state φ to the state ψ is equal to $|\psi^*\varphi|^2$.

3.2 The Main Postulate of Quantum Mechanics

The main postulate of quantum mechanics (which play the same role as Newtonian equations in classical mechanics) states:

For any physical object, it exists the Hermitian operator, $H = H^*$, such that the average value of any observable A satisfies the equation

$$\overline{\dot{A}} = \frac{i}{\hbar}\overline{(HA - AH)} + \overline{\frac{\partial A}{\partial t}} \,. \tag{3.1}$$

Here the left-hand side means

$$\overline{\dot{A}} \equiv \frac{d}{dt}\overline{A} = \langle\dot{\psi}|A|\psi\rangle + \langle\psi|\dot{A}|\psi\rangle + \langle\psi|A|\dot{\psi}\rangle \,, \tag{3.2}$$

and the right-hand side means

$$\frac{i}{\hbar}\overline{(HA - AH)} + \overline{\frac{\partial A}{\partial t}} = \frac{i}{\hbar}\langle\psi|HA - AH|\psi\rangle + \left\langle\psi\left|\frac{\partial A}{\partial t}\right|\psi\right\rangle . \tag{3.3}$$

H is called the Hamiltonian of the object. In a general case the form of H should be *guessed* for a given system. The main postulate may be satisfied by different methods. The following three methods (called *representations*) are used usually:

Schrödinger representation
Operators:

$$\dot{A}_S = \frac{\partial A_S}{\partial t} \,, \tag{3.4}$$

vectors:

$$i\hbar\frac{d}{dt}|\varphi_S\rangle = H|\varphi_S\rangle. \tag{3.5}$$

If the eigenvalue problem $H\varphi_S = E\varphi_S$ is solved, then

$$\varphi_S(t) = e^{-i\omega t}\varphi_S(0), \quad \text{where} \quad \omega = E/\hbar. \tag{3.6}$$

Heisenberg representation
Operators:

$$\dot{A}_H = \frac{i}{\hbar}(HA_H - A_H H) + \frac{\partial A_H}{\partial t} \,, \tag{3.7}$$

vectors:

$$\frac{d}{dt}|\varphi_H\rangle = 0. \tag{3.8}$$

When the eigenvalue problem $H\varphi_m^{(H)} = E_m\varphi_m^{(H)}$ is solved, then

$$\langle\varphi_j|A_H(t)|\varphi_k\rangle = e^{\frac{i}{\hbar}(E_j - E_k)t}\langle\varphi_j|A_S|\varphi_k\rangle \,. \tag{3.9}$$

Interaction representation
If the Hamiltonian is presented in the form

$$H = H_0 + V(t) \,, \tag{3.10}$$

then operators:

$$\dot{A}_I = \frac{i}{\hbar}(H_0 A_I - A_I H_0) + \frac{\partial A_I}{\partial t} \,, \tag{3.11}$$

vectors:

$$i\hbar\frac{d}{dt}|\varphi_I\rangle = V(t)\,|\varphi_I\rangle\,. \tag{3.12}$$

Coupling of different representations:

$$\varphi_S(t) = \mathcal{U}\varphi_H\,, \tag{3.13}$$

$$A_H(t) = \mathcal{U}^* A_S \mathcal{U}\,, \tag{3.14}$$

$$A_I(t) = e^{iH_0t}A_S e^{-iH_0t}\,, \tag{3.15}$$

where we introduced the evolution operator $\mathcal{U}(t) = e^{-i(H/\hbar)t}$.

3.3 Density Matrix Formalism

The *density operator* (matrix) $\mathcal{P}$, which *completely* characterizes the system state, is defined by the following set of axioms:

(1) $\mathcal{P}$ is Hermitian operator; $\mathcal{P} = \sum_j \omega_j |j\rangle\langle j|$, where $\mathcal{P}|j\rangle = \omega_j\,|j\rangle$.

(2) $\omega_j \geq 0$ ($\mathcal{P}$ is positively defined).

(3) $\sum_j \omega_j = 1$, or $\mathrm{Sp}\,\mathcal{P} = 1$.

(4) $\overline{A} = \mathrm{Sp}\,(\mathcal{P}A) = \sum_j \omega_j\,\langle j|A|j\rangle$. Here ω_j is the probability for the system to be in the state $|j\rangle$.

Note: in distinct from the wave function, the density matrix is defined *uniquely.*

Definition: The state is called the *pure state*, if only one $\omega_j = 1$, while all others $= 0$.

Theorem: The state is pure, if and only if $\mathcal{P}^2 = \mathcal{P}$, i.e. if $\mathcal{P}$ is the projection operator.

The main postulate of quantum mechanics takes the form

$$\mathrm{Sp}\,(\dot{A}\mathcal{P} + A\dot{\mathcal{P}}) = \mathrm{Sp}\,\left[\frac{i}{\hbar}(HA - AH)\mathcal{P} + \frac{\partial A}{\partial t}\mathcal{P}\right]. \tag{3.16}$$

In the Schrödinger representation from the axiom 1, using $|j(t)\rangle = e^{-iHt}|j(0)\rangle$, we obtain

$$\mathcal{P}(t) = e^{-iHt}\mathcal{P}(0)\,e^{+iHt}, \tag{3.17}$$

so that the density matrix satisfies the Liouville equation

$$\dot{\mathcal{P}} = -\frac{i}{\hbar}(H\mathcal{P} - \mathcal{P}H)\,. \tag{3.18}$$

In the Heisenberg representation $\mathcal{P}$ does not depend of time.
Applications:

$$\mathrm{Prob}\,(l) = \mathrm{Sp}\,(\mathcal{P}\cdot|l\rangle\langle l|) = \langle l|\mathcal{P}|l\rangle = \sum_j \omega_j\,|\langle l|j\rangle|^2. \tag{3.19}$$

Information entropy:

$$S = -\sum_j \omega_j\,\ln\omega_j = -\mathrm{Sp}\,(\mathcal{P}\ln\mathcal{P}) = -\overline{\ln\mathcal{P}}\,. \tag{3.20}$$

For a pure state we have $S = 0$, while for the equipartition distribution, $\omega_j = \text{const}$, S reaches its maximal value.

In the coordinate representation:

$$\mathcal{P}(x, x') = \sum_j \omega_j \, \varphi_j^*(x')\varphi_j(x)\,, \tag{3.21}$$

$$\overline{A} = \int dx\, dx' \; \mathcal{P}(x, x')\, A(x', x)\,, \tag{3.22}$$

$$\overline{x} = \int dx \; x\,\mathcal{P}(x, x)\,, \tag{3.23}$$

$$\overline{p} = -\int dx \; \left[-i\hbar\frac{\partial}{\partial x}\mathcal{P}(x, x')\right]_{x=x'}\,. \tag{3.24}$$

3.4 Conservation Laws

As was emphasized above, there are no general receipt how to involve a Hamiltonian for a given problem. In many cases it has to be guessed. Typically, the following procedure is used:
- first, we have to choose an appropriate Hilbert space;
- second, we have to guess a form of the Hamiltonian;
- finally, we have to choose a suitable representation and then solve the corresponding evolution equation.

Analogously to the classical mechanics, a very helpful is to use the system symmetry and the corresponding conservation laws.

Let us consider the conservative system, i.e. the system described by the Hamiltonian which does not depend implicitly on time. An observable A is conserved, if $\dot{\overline{A}} = 0$, or

$$\frac{d}{dt}\langle A\rangle = 0\,. \tag{3.25}$$

From the main postulate one can see that the condition (3.25) is satisfied for *any* state ψ, *if and only if*, first, A does not depend implicitly on time and, second, if A commutates with the Hamiltonian,

$$[A, H]_- = 0\,. \tag{3.26}$$

A conservation law is always connected with the corresponding symmetry of the system. A general theory is described below.

Let us define:
- Let G be the group of transformations of the system.
- Let P be the unitary representation of the group G in the space of vectors of the given system, $P(G) \equiv \{U\}$, where $U \in P(G)$ is the unitary operator corresponding to the element $g \in G$, i.e. the transformation g is described by $\psi \to U\psi$ and $A \to UAU^{-1}$.
- If every $U \in P(G)$ satisfies Eq. (3.26), then G is the *symmetry group* of the given system.
- Let A_G be the Lee algebra uniquely coupled with the symmetry group G.
- Let $\widetilde{P}$ be the representation of the algebra A_G in the space of vectors of the given system.

Then $\widetilde{P}(A_G) \equiv \{A\}$, where any $A \in \widetilde{P}(A_G)$ is the Hermitian operator, i.e. it is observable. Also, the corresponding unitary operator $U \in P(G)$ can be presented as

$$U = e^{i\alpha A}, \tag{3.27}$$

so that U describes a "shift" of the system state on the "distance" α (the reverse statement will be true if the system allows an infinitesimally small shifts α).

Let us consider the following examples.

(1) The trivial choice $A = -H/\hbar$ corresponds to energy conservation. The corresponding unitary operator is the *evolution operator*,

$$U = e^{-iHt/\hbar}, \tag{3.28}$$

it describes the shift of the system state along the time variable t,

$$|\psi_S(t)\rangle = U\,|\psi_S(0)\rangle, \tag{3.29}$$

or

$$B_H(t) = UB_H(0)\,U^{-1}. \tag{3.30}$$

(2) The choice $A = \mathbf{P}/\hbar$, where $\mathbf{P}$ is the total momentum of the system, corresponds to the momentum conservation due to translational invariance of the system. The corresponding unitary operator

$$U = e^{i\mathbf{aP}/\hbar} \tag{3.31}$$

describes the displacement of the center of mass of the system over the distance a,

$$|q + a\rangle_S = U\,|q\rangle_S, \tag{3.32}$$

or

$$(Q + a)_H = UQ_HU^{-1}. \tag{3.33}$$

(3) The choice $A = \mathbf{J}/\hbar$, where $\mathbf{J}$ is the total angular momentum of the system, corresponds to the angular momentum conservation due to rotational invariance of the system. The corresponding unitary operator

$$U = e^{i\phi\mathbf{nJ}/\hbar} \tag{3.34}$$

describes the rotation of the system on the angle ϕ over the axis $\mathbf{n}$. In a general case $\mathbf{J}$ is the sum of orbital and spin angular operators (see below Sec. 3.6).

(4) The *inversion operator* Π is defined by

$$\Pi|\mathbf{q}\rangle = |-\mathbf{q}\rangle\,. \tag{3.35}$$

The operator Π is the Hermitian unitary operator. Because $\Pi^2 = \mathbf{1}$, the eigenvalues of Π are ±1, i.e. $\Pi|\pm\rangle = \pm|\pm\rangle$, where $|\pm\rangle$ are the eigenvectors. Any state may be expanded over these two eigenvectors,

$$|\psi\rangle = |\psi_+\rangle + |\psi_-\rangle, \tag{3.36}$$

where $|\psi_+\rangle$ is the even component and $|\psi_-\rangle$ is the odd component. If an operator A commutes with Π, the eigenvectors of A should be either even or odd. For example, the eigenstates of the orbital momentum operator $\mathbf{L}$ behave as

$$\Pi Y_{lm}(\theta,\phi) = (-1)^l Y_{lm}(\theta,\phi)\,. \tag{3.37}$$

Any observable may be split into the even and odd operators, $A = A_+ + A_-$, where

$$\Pi A_+\Pi^* = A_+\,, \quad \Pi A_-\Pi^* = -A_-\,. \tag{3.38}$$

Table 3.1: Symmetry operators

symmetry group of	generators	rang	invariant operators
translation	$\mathbf{P}$	3	$\mathbf{P}$
inversion	Π	1	Π
rotation	$\mathbf{J}$	1	$\mathbf{J}^2$
rotation and inversion	$\mathbf{J}$, Π	2	$\mathbf{J}^2$, Π
translation and rotation	$\mathbf{J}$, $\mathbf{P}$	3	$\mathbf{P}^2$, $(\mathbf{J}\cdot\mathbf{P})$

The operators H, $\mathbf{L}$, $\mathbf{s}$, $\mathbf{J}$ are the even operators, while the operators $\mathbf{Q}$ and $\mathbf{P}$ are the odd operators. Note that

$$\langle\psi_\pm|A_-|\psi_\pm\rangle = 0\,. \tag{3.39}$$

Usually $[\Pi, H]_- = 0$; the corresponding conserved quantity is called the *parity* (notice that in the weak interaction of the quantum field theory the parity is not conserved). Thus, if an eigenstate of H is not degenerated, this state must have a certain parity. The matrix representation of Π is

$$\Pi = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{3.40}$$

The main symmetry operators are summarized in Table 3.1.

Let the symmetry group G (*i*) be the unitary semi-simple Lee group, (*ii*) have n generators, and (*iii*) have l invariant (Hermitian) operators ($l < n$). Then:
(1) the system has n conserved quantum numbers;
(2) the system has l “good” quantum numbers, which:
– conserve,
– can be measured simultaneously,
– uniquely define the multiplet, and
– the transitions are allowed only within the multiplet;
(3) all states of a given multiplet have the same energy.

3.5 Nonrelativistic Quantum Mechanics

The nonrelativistic quantum mechanics is based on the following *two main hypotheses*, which are consistent with the main postulate: the first is the shape of Hamiltonian,

$$H = \frac{P^2}{2m} + V(Q)\,, \tag{3.41}$$

and the second is the commutation rule,

$$QP - PQ = i\hbar\,, \tag{3.42}$$

where P is the momentum operator and Q is the coordinate operator. Therefore we have

$$P = m\dot{Q},$$

and for any *analytical* function f

$$f(Q_1, \ldots, Q_r, \ldots)\,P_r - P_r\,f(Q_1, \ldots, Q_r, \ldots) = i\hbar\frac{\partial f}{\partial Q_r}\,, \tag{3.43}$$

$$Q_r\, f(P_1,\ldots,P_r,\ldots) - f(P_1,\ldots,P_r,\ldots)\, Q_r = i\hbar \frac{\partial f}{\partial P_r}\,. \tag{3.44}$$

3.5.1 Schrödinger equation (conventional form)

Using the continuum coordinate basis $Q|q\rangle = q|q\rangle$, we obtain for the momentum operator the expression $P = -i\hbar\frac{\partial}{\partial Q}$. Introducing the wave function $\psi_E(q) = \langle q|E\rangle$, the equation $H|E\rangle = E|E\rangle$ may be rewritten in the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2}\psi_E(q) + V(q)\,\psi_E(q) = E\,\psi_E(q)\,. \tag{3.45}$$

3.6 Angular Momentum

As an important example of Hilbert space, let us consider the angular momentum.

Definition: The operator $\mathbf{M} = \{M_1, M_2, M_3\}$ is called the *angular momentum operator*, if it satisfies the equation

$$\mathbf{M} \times \mathbf{M} = i\hbar\mathbf{M}\,. \tag{3.46}$$

Theorem: (?) one of the components of the angular momentum operator, say M_3, always may be chosen in such a way that

$$[M_3, \mathbf{M}^2]_- = 0\,. \tag{3.47}$$

Let $|m, m_3\rangle$ be an eigenvector of both operators $\mathbf{M}^2$ and M_3. Then

$$M_3|m, m_3\rangle = \hbar m_3|m, m_3\rangle \tag{3.48}$$

and

$$\mathbf{M}^2|m, m_3\rangle = \hbar^2 m(m+1)|m, m_3\rangle, \tag{3.49}$$

where

$$m = 0,\ \frac{1}{2},\ 1,\ \frac{3}{2},\ 2,\ \ldots \tag{3.50}$$

(this sequence may either be finite or may continue up to infinity), and

$$m_3 = \underbrace{-m, -m+1, \ldots, m-1, m}_{2m+1}\,. \tag{3.51}$$

3.6.1 Orbital momentum

The orbital momentum is defined as $\mathbf{L} = \mathbf{Q} \times \mathbf{P}$,

$$\begin{aligned} L_1 &= Q_2P_3 - Q_3P_2\,, \\ L_2 &= Q_3P_1 - Q_1P_3\,, \\ L_3 &= Q_1P_2 - Q_2P_1 \end{aligned} \tag{3.52}$$

analogously as in classical mechanics. Its eigenvectors/eigenvalues are

$$\mathbf{L}^2|l, l_3\rangle = \hbar^2 l(l+1)|l, l_3\rangle\,, \tag{3.53}$$

where $l = 0, 1, 2, \ldots \infty$.

In the coordinate representation (r, θ, φ):

$$L_z = -i\frac{\partial}{\partial\varphi}\,, \tag{3.54}$$

$$\mathbf{L}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \tag{3.55}$$

and

$$|l, m\rangle = \int_0^{\pi} d\theta\,\sin\theta \int_0^{2\pi} d\varphi\, Y_{l,m}(\theta,\varphi)\,|\theta,\varphi\rangle\,. \tag{3.56}$$

Here

$$Y_{l,\,m}(\theta,\varphi) = \left\{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right\}^{1/2} P_l^m(\cos\theta)\, e^{im\varphi}. \tag{3.57}$$

In particular,

$$Y_{0,\,0} = \frac{1}{\sqrt{4\pi}}\,, \tag{3.58}$$

$$Y_{1,\,1} = \sqrt{\frac{3}{4\pi}}\,\sin\theta\, e^{i\varphi}, \tag{3.59}$$

$$Y_{1,\,0} = \sqrt{\frac{3}{4\pi}}\,\cos\theta\,, \tag{3.60}$$

$$Y_{2,\,2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\sin(2\theta)\, e^{2i\varphi}, \tag{3.61}$$

$$Y_{2,\,1} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\sin(2\theta)\, e^{i\varphi}, \tag{3.62}$$

$$Y_{2,\,0} = \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) \tag{3.63}$$

and

$$Y_{l,-m} = Y_{l,m}^*\,. \tag{3.64}$$

Notice that $\sum_{l=0}^{L}(2l+1) = (L+1)^2$.

Note: the magnetic momentum of a charge, which is coupled with the orbital (mechanical) momentum L, is equal to $\mu_B m$, where $\mu_B = ...$ is ...

3.6.2 Spin momentum

Spin 0

This case is trivial, $\mathbf{s} = \mathbf{0}$.

Spin 1/2

For the spin-$\frac{1}{2}$ particles the spin operator is expressed throughout the Pauli matrices,

$$\mathbf{s} = \frac{1}{2}\hbar\sigma\,. \tag{3.65}$$

Recall that the Pauli matrices are defined as

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3.66}$$

In the coordinate representation

$$\sigma_{\theta\varphi} = \begin{pmatrix} \cos\theta & e^{-i\varphi}\sin\theta \\ e^{i\varphi}\sin\theta & -\cos\theta \end{pmatrix} = \sigma_1 \sin\theta\cos\varphi + \sigma_2 \sin\theta\sin\varphi + \sigma_3\cos\theta, \tag{3.67}$$

$$|\theta,\varphi;\uparrow\rangle = \begin{pmatrix} \cos\theta/2 \\ e^{i\varphi}\sin\theta/2 \end{pmatrix}, \quad |\theta,\varphi;\downarrow\rangle = \begin{pmatrix} -e^{-i\varphi}\sin\theta/2 \\ \cos\theta/2 \end{pmatrix}, \tag{3.68}$$

so that

$$\sigma_{\theta\varphi}|\theta,\varphi;\uparrow\rangle = +|\theta,\varphi;\uparrow\rangle\,, \quad \sigma_{\theta\varphi}|\theta,\varphi;\downarrow\rangle = -|\theta,\varphi;\downarrow\rangle\,. \tag{3.69}$$

Spin 1

For the spin-1 particles the spin operator is expressed throughout the Dirac matrices,

$$\mathbf{s} = \hbar\beta\,. \tag{3.70}$$

Recall that the Dirac matrices are

$$\beta_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \beta_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \beta_3 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{3.71}$$

In the coordinate representation

$$\beta_{\theta\varphi} = \frac{1}{\sqrt{2}}\begin{pmatrix} \sqrt{2}\,\cos\theta & e^{-i\varphi}\sin\theta & 0 \\ e^{i\varphi}\sin\theta & 0 & e^{-i\varphi}\sin\theta \\ 0 & e^{i\varphi}\sin\theta & -\sqrt{2}\,\cos\theta \end{pmatrix} \tag{3.72}$$

$$= \beta_1 \sin\theta\,\cos\varphi + \beta_2\sin\theta\,\sin\varphi + \beta_3\cos\theta, \tag{3.73}$$

$$|\theta,\varphi;+1\rangle = \begin{pmatrix} e^{-i\varphi}(1+\cos\theta) \\ \sqrt{2}\,\sin\theta \\ e^{i\varphi}(1-\cos\theta) \end{pmatrix}, \tag{3.74}$$

$$|\theta,\varphi;0\rangle = \begin{pmatrix} -e^{-i\varphi}\sin\theta \\ \sqrt{2}\cos\theta \\ e^{i\varphi}\sin\theta \end{pmatrix}, \tag{3.75}$$

$$|\theta,\varphi;-1\rangle = \begin{pmatrix} -e^{-i\varphi}(1-\cos\theta) \\ \sqrt{2}\,\sin\theta \\ -e^{i\varphi}(1+\cos\theta) \end{pmatrix}. \tag{3.76}$$

3.6.3 Total momentum

The total momentum is

$$\mathbf{J} = \mathbf{L} + \mathbf{S}\,. \tag{3.77}$$

Theorem: If the system consists of parts with the momenta $\mathbf{J_1}, \mathbf{J_2}, \ldots$, then the total momentum is $\mathbf{J} = \mathbf{J_1} + \mathbf{J_2} + \ldots$

3.7 Heisenberg Uncertainly Principle

Let the system is in a state $|b\rangle$, $\langle b|b\rangle = 1$, and denote

$$q = \langle b|Q|b\rangle\,, \tag{3.78}$$

$$p = \langle b|P|b\rangle\,, \tag{3.79}$$

$$(\Delta q)^2 = \langle b|(Q-q)^2|b\rangle\,, \tag{3.80}$$

$$(\Delta p)^2 = \langle b|(P-p)^2|b\rangle\,. \tag{3.81}$$

Theorem:

$$\Delta p\;\Delta q \geq \frac{1}{2}\hbar\,, \tag{3.82}$$

where the equality sign is realized for the harmonic oscillator only.

Proof: define

$$|u\rangle = (P-p)\,|b\rangle \quad \text{and} \quad |v\rangle = (Q-q)\,|b\rangle\,, \tag{3.83}$$

and then use the BS (?) inequality

$$\|u\| \cdot \|v\| \geq |\langle u|v\rangle|\,. \tag{3.84}$$

The equality is achieved, if and only if $|u\rangle = i\gamma|v\rangle$ with γ being real. The wave function in this case is Gaussian,

$$\psi_b(x) = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left[-\frac{\gamma}{2}(x-q)^2 + ipx\right]. \tag{3.85}$$

A general case: if there are three Hermitian operators K, L, and M such that

$$[K, L]_- = iM\,, \tag{3.86}$$

then

$$\overline{(\Delta K)^2}\,\overline{(\Delta L)^2} \geq \frac{1}{4}\overline{M^2}. \tag{3.87}$$

3.8 The HellmannFeynman Theorem

If

$$H = H_0 + gV, \tag{3.88}$$

then

$$E_0^{\text{exact}} = \langle \Psi_0(g)|H|\Psi_0(g)\rangle = E_0 + \int_0^g dg\,\frac{E_{\text{int}}(g)}{g}\,, \tag{3.89}$$

where $E_{\text{int}}(g) = \langle \Psi_0(g)|gV|\Psi_0(g)\rangle$. Thus,

$$\Delta E = \int_0^1 dg\,\langle \Psi_0(g)|V|\Psi_0(g)\rangle\,. \tag{3.90}$$

3.9 System of Identical Particles

Let us consider now a system of *identical* particles. The main point here is that in quantum mechanics, in contrast to classical mechanics, identical particles cannot be distinguished. This leads to the existence of Fermi and Bose types of particles.

First, we have to introduce a Hilbert space L_N for the system of N identical particles. It is natural to construct L_N using the Hilbert space $L_1 \equiv \{\psi_i^{(1)}\}$, the one-particle space. For example, for the system of two particles the Hilbert space $L_2 \equiv \{\psi^{(2)}\}$ may be constructed as the direct product of two one-particle spaces, $L_2 = L_1 \bigotimes L_1$, i.e. its elements are $\psi_{ij}^{(2)}(1,2) = \psi_i^{(1)}(1)\,\psi_j^{(1)}(2)$. But this space is *overcomplete* in the case of the system of identical particles. Indeed, the permutation $1 \Leftrightarrow 2$ must give the same state of the system, because the particles are identical. Therefore, it must be $\psi^{(2)}(2,1) = e^{i\beta}\psi^{(2)}(1,2)$ with β being real. Any choice for β may in principle be used, but only the following two choices, $\beta = 0$ and $\beta = \pi$, are realized in nature. The first one corresponds to Bose particles,

$$\psi^{(2)}(2,1) = +\psi^{(2)}(1,2), \tag{3.91}$$

and the second describes Fermi particles,

$$\psi^{(2)}(2,1) = -\psi^{(2)}(1,2). \tag{3.92}$$

The type of particles is connected with their spin: the particles with integer spin, $s = 0,\ 1,\ 2,\ \ldots$, are Bose particles, while the particles with half-integer spin, $s = \frac{1}{2},\ \frac{3}{2},\ \ldots$, are Fermi particles. The coupling of spin and type follows from the symmetry reason: the orbital momentum should be even for the symmetric wavefunction (for bosons) and odd for the antisymmetric wavefunction (for fermions). Because the orbital momentum is the sum of angular and spin momentums, that gives ... `see Lipkin p.158.`

Now let us consider a general case of $N \geq 2$ in more details.

3.9.1 Coordinate representation

To satisfy the condition (3.91) for the system of Bose particles, the wavefunction should be taken in the form

$$\psi_{i_1 i_2 \ldots i_N}^{(N)}(r_1, r_2, \ldots, r_N) = \mathcal{N} \sum \psi_{i_1}^{(1)}(r_1)\psi_{i_2}^{(1)}(r_2)\ldots\psi_{i_N}^{(1)}(r_N)\,, \tag{3.93}$$

where $\mathcal{N}$ is the normalization factor. For the Fermi system, we have to choose

$$\psi_{i_1 i_2}^{(2)}(r_1, r_2) = \frac{1}{\sqrt{2}}\left[\psi_{i_1}^{(1)}(r_1)\psi_{i_2}^{(1)}(r_2) - \psi_{i_1}^{(1)}(r_2)\psi_{i_2}^{(1)}(r_1)\right], \tag{3.94}$$

or, in a general case,

$$\psi_{i_1 i_2 \ldots i_N}^{(N)}(r_1, r_2, \ldots, r_N) = \mathcal{N} \sum_P (-1)^P \psi_{i_1}^{(1)}(r_1)\psi_{i_2}^{(1)}(r_2)\ldots\psi_{i_N}^{(1)}(r_N)\,. \tag{3.95}$$

This wavefunction may be written as the *Slater determinant*,

$$\psi_{i_1 i_2 \ldots i_N}^{(N)}(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_{i_1}^{(1)}(r_1) & \psi_{i_2}^{(1)}(r_1) & \ldots & \psi_{i_N}^{(1)}(r_1) \\ \psi_{i_1}^{(1)}(r_2) & \psi_{i_2}^{(1)}(r_2) & \ldots & \psi_{i_N}^{(1)}(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_1}^{(1)}(r_N) & \psi_{i_2}^{(1)}(r_N) & \ldots & \psi_{i_N}^{(1)}(r_N) \end{pmatrix}. \tag{3.96}$$

However, using of these wavefunctions in calculation is quite inconvenient, especially if the number of particles is not constant; much more natural and convenient is the canonical quantization basis introduced above in Sec. 2.4.

3.9.2 Canonical quantization basis

The vacuum state and creation-annihilation operators have been described above in Sec. 2.4. Any operator (e.g., observable) may be expressed through the creation and annihilation operators. In particular, the operator of the number of particles in a state $|i\rangle$ is $N_i = c_i^* c_i$, and the operator of the total number of particles is $N = \sum_i N_i$. A general form of a one-particle operator is

$$A = \sum_{ij} A_{ij} \, c_i^* c_j \, , \tag{3.97}$$

and a general form of a two-particle operator is

$$B = \sum_{iklm} B_{iklm} \, c_k^* c_i^* c_l c_m \, . \tag{3.98}$$

Clearly, the system Hamiltonian may be expressed through the creation–annihilation operators as well. In the simplest case, when the basis is constructed of eigenvectors of H, $H|i\rangle = \varepsilon_i |i\rangle$, and the interaction between the particles is absent, the Hamiltonian takes the form

$$H = \sum_i \varepsilon_i \, c_i^* c_i \, . \tag{3.99}$$

In a general case, a form of the Hamiltonian is to be guessed. But for the conventional Hamiltonian,

$$H = \sum_{a=1}^{N} \frac{p_a^2}{2m} + \sum_{a=1}^{N} V(x_a) + \frac{1}{2} \sum_{a \neq a'} v(x_a, x_{a'}) \, , \tag{3.100}$$

the transformation to the canonical quantization basis may be done with the following unique receipt. Namely, let us choose a one-particle basis $\{\varphi_i(x)\}$ and then introduce the so-called *field operator*

$$\Psi(x) = \sum_i c_i \, \varphi_i(x) \, . \tag{3.101}$$

Then a one-particle operator $A = \sum_{a=1}^{N} A(x_a)$ in the canonical quantization basis is defined by

$$A = \langle \Psi^*(x) A(x) \Psi(x) \rangle = \sum_{ij} \langle \varphi_i | A(x) | \varphi_j \rangle \, c_i^* c_j \, , \tag{3.102}$$

and the two-particle operator $B = \frac{1}{2} \sum_{a \neq a'} B(x_a, x_{a'})$ is defined by

$$B = \frac{1}{2} \langle \Psi^*(x) \Psi^*(x') B(x, x') \Psi(x') \Psi(x) \rangle = \sum_{iklm} B_{iklm} \, c_k^* c_i^* c_l c_m \, , \tag{3.103}$$

where

$$B_{iklm} = \int dx \int dx' \; \varphi_i^*(x) \varphi_k^*(x') B(x, x') \varphi_l(x) \varphi_m(x') \, . \tag{3.104}$$

One can easily check that the matrix elements of operators defined in this way, coincide with the correct ones.

The main trick in calculation of matrix elements in the canonical quantization basis is the following: using commutation relations, we should move the annihilation operators one by one to the right-hand side (or the creation operators, to the left-hand side); then their action on the vacuum state gives zero, while constants arising during the permutations, give the result.

Finally note that when there are two different types of particles, e.g. electrons and protons, the former described by operators c, and the later, by operators d, for the mixed commutations we may use either commutation or anticommutation relation depending on which is more convenient; in both cases the mixing commutators must be taken to be zero (see Lipkin p.175).

3.9.3 Nonortogonal basis (Fermi system)

In some cases, a more clear physics is achieved with using a nonortonormalized basis $\{\phi_i\}$,

$$\langle\phi_i|\phi_j\rangle = S_{ij}\,, \quad \{S_{ij}\} \equiv \mathbf{S}\,. \tag{3.105}$$

Introducing the creation and annihilation operators a_i^* and a_i with the help of the field operator

$$\Psi = \sum_i \phi_i a_i\,, \tag{3.106}$$

one can find that they must satisfy the commutation relation

$$[a_i^*, a_j]_+ = \left(\mathbf{S}^{-1}\right)_{ji}\,. \tag{3.107}$$

Then, the one-particle operators still have the standard form,

$$A = \sum_{kl} \langle\phi_k|A|\phi_l\rangle\, a_k^* a_l\,. \tag{3.108}$$

the identity operator now takes the form

$$\mathbf{1} = \sum_{kl\sigma} |\phi_{k\sigma}\rangle S_{kl}^{-1} \langle\phi_{l\sigma}|\,, \tag{3.109}$$

and the operator of the total number of particles is

$$N = \sum_{kl\sigma} a_{k\sigma}^*\, S_{kl}\, a_{l\sigma}\,. \tag{3.110}$$

The operator a_i^* creates a particle in the state with the wavefunction $\sum_m \phi_m S_{mi}^{-1}$ which is orthogonal to all functions ϕ_k with $k \neq i$. On the other hand, the particle in the state with the wavefunction ϕ_m is created by the operator $\sum_k S_{mk} a_k^*$.

3.10 Examples

3.10.1 Harmonic oscillator

The harmonic oscillator is the most important system in quantum mechanics (as well as in classical mechanics, where it corresponds to linear approximation, the main lowest-order approximation). Besides, the harmonic oscillator is the only system which has the same description in quantum and classical mechanics.

Coordinate representation

In the coordinate (conventional) representation, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+\frac{1}{2}m\omega_0^2x^2\psi=E\psi(x)\,, \tag{3.111}$$

which has the solution

$$\psi_n(x)=\left(\frac{m\omega_0}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}\,\exp\left(-\frac{m\omega_0}{2\hbar}x^2\right)H_n\left(x\sqrt{\frac{m\omega_0}{\hbar}}\right), \tag{3.112}$$

where

$$H_n(y)=(-1)^n e^{y^2}\frac{d^n}{dy^n}e^{-y^2} \tag{3.113}$$

are Hermite polynomials. The spectrum of harmonic oscillator is discrete, infinite, and equidistant,

$$E_n=\left(n+\frac{1}{2}\right)\hbar\omega_0\,,\quad n=0,\,1,\,2,\,\ldots,\infty. \tag{3.114}$$

The "dipole" matrix elements are

$$x_{mn}=\int dx\,\psi_n^* x\psi_m=\delta_{n,m+1}\sqrt{\frac{n\hbar}{2m\omega_0}}+\delta_{n,m-1}\sqrt{\frac{(n+1)\hbar}{2m\omega_0}}\,. \tag{3.115}$$

Note: for a general case, $H=a^2p^2+b^2x^2$, the spectrum is $E_n=\left(n+\frac{1}{2}\right)\hbar(2ab)$.

Canonical quantization basis

In the canonical quantization basis the description of harmonic oscillator takes a much simpler form, because we do not need to solve the partial differential equation and to know the explicit form of wavefunctions. The creation operator may be introduced as

$$c^*=\left(\frac{m}{2\hbar\omega_0}\right)^{1/2}\left(\omega_0\,x-\frac{i}{m}p\right). \tag{3.116}$$

From the commutation relation $xp-px=i\hbar$ it follows that c and c^* satisfy the Bose commutation $cc^*-c^*c=1$. Then, reversing (3.116),

$$x=\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}(c+c^*)\,, \tag{3.117}$$

and then substituting (3.116) and (3.117) into the Hamiltonian

$$H=\frac{p^2}{2m}+\frac{1}{2}m\omega_0^2x^2, \tag{3.118}$$

we immediately obtain

$$H=\hbar\omega_0\left(c^*c+\frac{1}{2}\right). \tag{3.119}$$

Thus, the harmonic oscillator may be treated either as one particle with the equidistant spectrum, or as the system of identical noninteracting Bose particles with *zero rest mass*, so that their number is not conserved; these descriptions are identical.

3.10.2 A free particle

Let us consider now the simplest case of $V(\mathbf{r}) \equiv 0$. In the three-dimensional space, there are three conserved quantities, so that a state is to be labelled by three quantum numbers. Depending on a symmetry of the problem, one may use different bases. All the bases belong to continuum spectrum, $E \geq 0$, therefore they are normalized on delta-function.

Plane waves

The simplest is the basis of plane waves,

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = \psi_{\mathbf{k}}(\mathbf{r})\, e^{-i\frac{E}{\hbar}t}, \quad \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{3.120}$$

the states are labelled by the quantum numbers $\mathbf{k} = \{k_x, k_y, k_z\}$. These functions are eigenfunctions of the momentum operator $\mathbf{P}$ which commutates with the Hamiltonian. The energy is

$$E = \frac{\hbar^2}{2m}\mathbf{k}^2 = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)\,. \tag{3.121}$$

Spherical symmetry

When the problem has a spherical symmetry, we may use for the basis the eigenfunctions of the angular momentum operator $\mathbf{L}$ (which commutates with the Hamiltonian). The states are labelled by three quantum numbers E, l, and m (instead of E one might use $k = \sqrt{2mE}/\hbar$). The wave functions are

$$\psi_{k,\,l,\,m}(r, \theta, \varphi) = R^0_{k,\,l}(r)\, Y_{l,\,m}(\theta, \varphi)\,, \tag{3.122}$$

where

$$R^0_{k,\,l}(r) = \frac{\chi^0_{k,\,l}(r)}{r}\;, \quad \chi^0_{k,\,l}(r) = \sqrt{kr}\, J_{l+\frac{1}{2}}(kr)\,, \tag{3.123}$$

and J is the Bessel function. The wave functions are normalized on delta-function, so that

$$\int dr\; \chi^0_{k',\,l}(r)\; \chi^0_{k,\,l}(r) = \delta(k' - k)\,. \tag{3.124}$$

The state $R^0_{k,\,l}(r)$ corresponds to the standing wave. Besides, in scattering problem, the propagating waves are also used,

$$R^{\pm}_{k,\,l}(r) = \sqrt{\frac{m}{k\hbar}}\,(-1)^l \left(\frac{r}{k}\right)^l \left(\frac{d}{r\,dr}\right)^l \frac{e^{\pm ikr}}{r}\;, \tag{3.125}$$

where the sign $+$ $(-)$ corresponds to the wave outgoing from the center (coming to the center). The wave functions $\psi^{\pm}$ are normalized on one outgoing (incoming) particle per one time unit.

The plane wave may be expanded in a series over the spherical (Bessel) wavefunctions,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} \sqrt{\frac{\pi}{2}}\, i^l (2l+1)\, P_l(\cos\theta)\, \frac{J_{l+\frac{1}{2}}(kr)}{kr}\;, \tag{3.126}$$

where P are the Legendre polynomials,

$$P_l^m(x) = \frac{(1-x^2)^{m/2}}{2^l l!} \frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l. \tag{3.127}$$

Some particular cases:

$$R^0_{k,0}(r) = \sqrt{\frac{2}{\pi}}\,\frac{\sin(kr)}{r}\,, \tag{3.128}$$

$$R^0_{k,1}(r) = \sqrt{\frac{2}{\pi}}\,k\left[\frac{\sin(kr)}{(kr)^2} - \frac{\cos(kr)}{kr}\right], \tag{3.129}$$

$$R^0_{k,2}(r) = \sqrt{\frac{2}{\pi}}\,k\left\{\left[\frac{3}{(kr)^3} - \frac{1}{kr}\right]\sin(kr) - 3\frac{\cos(kr)}{(kr)^2}\right\}, \tag{3.130}$$

$$R^{\pm}_{k,0}(r) = \sqrt{\frac{m}{k\hbar}}\,\frac{e^{\pm ikr}}{r}\,. \tag{3.131}$$

Asymptotic for $r \to 0$:

$$R^0_{k,l}(r) \approx r^l\sqrt{\frac{2}{\pi}}\,\frac{k^{l+1}}{(2l+1)!!}\,, \tag{3.132}$$

$$R^{\pm}_{k,l}(r) \approx r^{-(l+1)}\sqrt{\frac{m}{k\hbar}}\,\frac{(2l-1)!!}{k^l}\,. \tag{3.133}$$

Asymptotic for $r \to \infty$:

$$R^0_{k,l}(r) \approx \sqrt{\frac{2}{\pi}}\,\frac{\sin(kr - l\pi/2)}{r}\,, \tag{3.134}$$

$$e^{ikr\cos\theta} \approx \frac{1}{kr}\sum_{l=0}^{\infty} i^l(2l+1)\,P_l(\cos\theta)\,\sin\left(kr - \frac{l\pi}{2}\right), \tag{3.135}$$

$$R^{\pm}_{k,l}(r) \approx \sqrt{\frac{m}{k\hbar}}\,\frac{\exp\left[\pm i\,(kr - l\pi/2)\right]}{r}\,. \tag{3.136}$$

Cylindrical symmetry

When the system has a cylindrical symmetry, the cylindrical Bessel functions are used:

$$e^{ikr\cos\theta} = \sum_{m=-\infty}^{\infty} J_m(kr)\,i^m e^{-im\theta} \tag{3.137}$$

$$= J_0(kr) + 2\sum_{k=1}^{\infty}(-1)^k\left\{J_{2k}(kr)\cos(2k\theta) + iJ_{2k-1}(kr)\cos[(2k-1)\theta]\right\}. \tag{3.138}$$

Note: the bases describe above, are complete for the $V(\mathbf{r}) \geq 0$ case, but not so if $V(\mathbf{r}) < 0$ somewhere; in the latter case the basis should additionally be completed with coupled (discrete) state(s), described by localized wavefunctions.

3.10.3 Central-symmetry potential

When the potential $U(r)$ has the central symmetry, the Hamiltonian commutates with the angular momentum operator. Thus, the states may be labelled by the energy E and by the eigenvalues l and m of the operators $\mathbf{L}$ and L_z (the direction z may be chosen arbitrary). Writing

$$\psi = R_l(r)\,Y_{l,m}(\theta,\varphi) \tag{3.139}$$

and introducing the function

$$\chi_l(r) = rR_l(r), \tag{3.140}$$

where $\chi_l(r) \to 0$ at $r \to 0$, we obtain for $\chi_l(r)$ the equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\chi_l(r) + \left[rU_l(r)\frac{1}{r}\right]\chi_l(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\chi_l(r) = E\chi_l(r)\,. \tag{3.141}$$

In Eq. (3.141) we wrote $U_l(r)$ for a general (pseudopotential) case ...

Coulomb potential

Let us consider the potential $U(r) = \mp\alpha/r$, where $\alpha > 0$. The states in the continuous spectrum, $E > 0$, are labelled by the quantum number k and has the asymptotic (standing waves) at $r \to \infty$

$$R_{k,\,l}(r) \approx \sqrt{\frac{2}{\pi}}\,\frac{1}{r}\sin\left(kr \pm \frac{1}{k}\ln(2kr) - \frac{l\pi}{2} + \delta_l\right), \tag{3.142}$$

where

$$\delta_l = \arg\Gamma\left(l + 1 \mp \frac{i}{k}\right). \tag{3.143}$$

The coupled states, $E < 0$, exist for the case of attraction only. They consist of the discrete spectrum and may be labelled by the quantum number n. Note that for the Coulomb attraction, the number of coupled states is infinite at any α, and $E_n \to -0$ at $n \to \infty$.

Power potential

Now let us consider the potential $U(r) = \pm\alpha/r^n$ with $n > 1$. Let for simplicity $U(r) = 0$ at $r > R_0$ (R_0 is the radius of interaction).

For the continuous spectrum, $E > 0$, in the region $r > R_0$ the wave function is determined by the equation

$$\chi''_{k,\,l}(r) - \frac{l(l+1)}{r^2}\chi_{k,\,l}(r) + k^2\chi_{k,\,l}(r) = 0\,, \tag{3.144}$$

which has the solution

$$\chi_{k,\,l}(r) = \mathcal{N}\sqrt{kr}\left[\cos\delta_l(k)\; J_{l+\frac{1}{2}}(kr) - \sin\delta_l(k)\; N_{l+\frac{1}{2}}(kr)\right], \tag{3.145}$$

where $\mathcal{N}$ is the normalization constant and N is the Neumann function. The wavefunction has the following asymptotic at $r \to \infty$,

$$R_{k,\,l}(r) \approx \mathcal{N}\,\frac{\sin\left(kr - l\pi/2 + \delta_l(k)\right)}{r}\,. \tag{3.146}$$

The phase $\delta_l(k)$ is defined by matching the function (3.145) with the solution of the Schrödinger equation in the region $r < R_0$.

The coupled states, $E < 0$, exist only for the case of attraction, and this attraction should be strong enough, $\alpha \sim R_0^{-2}$ (?). In the region $r > R_0$ the wave function is determined by the equation

$$\chi''_{k,\,l}(r) - \frac{l(l+1)}{r^2}\chi_{k,\,l}(r) - \kappa^2\chi_{k,\,l}(r) = 0\,, \tag{3.147}$$

which, in particular, at $l = 0$ has the solution

$$\chi_{k,\,0}(r) = \mathcal{N}e^{-\kappa r}. \tag{3.148}$$

The parameter κ is defined by matching the function (8.14) with the solution of the Schrödinger equation in the region $r < R_0$. It has only a finite number of solutions, which define the discrete system spectrum, $E_n = -\hbar^2\kappa_n^2/2m$.

3.10.4 Hydrogen atom

The Hydrogen atom is one of few exactly solvable systems in quantum mechanics. The Schrödinger equation $(c > 0)$

$$-\frac{\hbar^2}{2m}\Delta\psi - \frac{2c}{r}\psi = E\psi(\mathbf{r}) \tag{3.149}$$

has, besides the continuous spectrum solutions described above in Sec. 3.10.3, the infinite discrete number of bounded solutions

$$\psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r)\, Y_{l,m}(\theta,\varphi)\,, \tag{3.150}$$

$$R_{n,l}(r) = -\frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{[(n+l)!]^3}}\; e^{-r/n}\left(\frac{2r}{n}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{n}\right), \tag{3.151}$$

where

$$L_n^m(z) = \frac{n!}{(n-m)!}\; e^z \frac{d^n}{dz^n} e^{-z} z^{n-m} \tag{3.152}$$

are the Laguerre polynomials.

The states are labelled by three quantum number n, l and m, which vary within the intervals

$$\begin{aligned} n &= 1,\, 2,\, \ldots,\, \infty\,, \\ l &= 0,\, 1,\, 2,\, \ldots,\, n-1, \\ m &= -l, -l+1,\, \ldots,\, l-1,\, l. \end{aligned} \tag{3.153}$$

The energy of these states depends on the main quantum number only:

$$E_n = -\frac{2mc^2}{n^2\hbar^2}\;. \tag{3.154}$$

A degeneracy over l is “accidental”, it exists for the Coulomb potential only, i.e. only for the hydrogen atom (and when other perturbations like relativistic ones may be ignored). For any deviation from the Coulomb law, the energy of a state depends on l. In atomic physics the states with different l are often labelled by letters in the following way:

$$\begin{array}{lll} l=0 & \text{corresponds to} & \text{s} \\ l=1 & \text{corresponds to} & \text{p} \\ l=2 & \text{corresponds to} & \text{d} \\ l=3 & \text{corresponds to} & \text{f} \\ \ldots & & \end{array} \tag{3.155}$$

Thus, the Hilbert space for the Hydrogen atom is $L = L_r \bigotimes L_\theta \bigotimes L_\varphi \bigotimes L_\sigma$, where L_r is the set of Laguerre polynomials of r, L_θ is the set of Hermite polynomials of $\cos\theta$, L_φ is the Fourier functions of φ, and L_σ consists of two vectors $|\uparrow\rangle$ and $|\downarrow\rangle$. This basis is complete and, therefore, may be used in studying of more complicated atoms as well. The basis of L_r is, however, to be modified — in computer calculation the Hermitian polynomials might be more convenient, because the calculation of matrix elements becomes simpler. The ground state of ...

$$|1s\uparrow, 1s\downarrow, 2s\uparrow, 2s\downarrow, 2p_x\uparrow, 2p_x\downarrow, 2p_y\uparrow, 2p_y\downarrow, 2p_z\uparrow, 2p_z\downarrow, 3s\uparrow, 3s\downarrow, 0, 0, \ldots\rangle. \tag{3.156}$$

3.10.5 Free (noninteracting) Fermi gas

For the free electron gas the natural basis consists of plane waves,

$$\varphi_k(\mathbf{r}) = |\mathbf{k}\rangle = V_{\mathrm{vol}}^{-1/2} e^{i\mathbf{kr}}, \tag{3.157}$$

which are numerated by the wavevector

$$\mathbf{k} = \left(\frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right). \tag{3.158}$$

The energy of the state $|\mathbf{k}\rangle$ is

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}. \tag{3.159}$$

The field operator has the form

$$\Psi(r) = \sum_{k\sigma} c_{k\sigma}\, \varphi_k(\mathbf{r})\, |\sigma\rangle, \tag{3.160}$$

so that the Hamiltonian takes the form

$$H_0 = \sum_{k\sigma} \varepsilon_k\, c^*_{k\sigma} c_{k\sigma}. \tag{3.161}$$

In the ground state (GS) of the system $|\Phi_0\rangle$ the electrons occupy all levels below the Fermi level, the energy of which is determined by the total number of electrons:

$$N = \sum_{|k|<k_F,\sigma} 1 = 2(\text{spin}) \frac{V_{\mathrm{vol}}}{(2\pi)^3} \int_{|k|<k_F} d^3k\, 1 = 2 \frac{V_{\mathrm{vol}}}{(2\pi)^3} \frac{4}{3} \pi k_F^3 \tag{3.162}$$

so that

$$k_F = \left(3\pi^2 \frac{N}{V_{\mathrm{vol}}} \right)^{1/3}, \quad \epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V_{\mathrm{vol}}} \right)^{2/3}, \tag{3.163}$$

and the GS energy is determined by the *kinetic energy* of all electrons below the Fermi level,

$$\begin{aligned} E_0 &= 2 \frac{V_{\mathrm{vol}}}{(2\pi)^3} 4\pi \frac{\hbar^2}{2m} \int_0^{k_F} dk\, k^4 = V_{\mathrm{vol}} \frac{\hbar^2 k_F^5}{10\pi^2 m} = N \frac{3}{5} \epsilon_F \\ &= \frac{3\hbar^2}{10m} \left(\frac{3\pi^2}{V_{\mathrm{vol}}} \right)^{2/3} N^{5/3} = N \frac{1}{r_s^2} \frac{3\hbar^2}{10m} \left(\frac{9\pi}{4} \right)^{2/3} =? = \frac{2.21}{r_s^2}\ (\text{Ry}). \end{aligned} \tag{3.164}$$

Note also a useful formula

$$d^3k = 4\pi k^2\, dk = 2\pi \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon}\, d\epsilon. \tag{3.165}$$

Excitations over the GS are defined as follows: let us introduce the quasiparticle annihilation operator η_k defined by the equation $\eta_k |\Phi_0\rangle = 0$ (for all k!), i.e.

$$\eta_k = \begin{cases} c_k & \text{for} \quad k > k_F \quad \text{(electron)}, \\ c_k^* & \text{for} \quad k < k_F \quad \text{(hole)}. \end{cases} \tag{3.166}$$

Then the creation operator is η_k^*, and the main operators take the form

$$N_{\text{quasiparticles}} = \sum_{k\sigma} \eta_{k\sigma}^* \eta_{k\sigma} = N_{\text{el}} + N_{\text{holes}} \; ,$$
$$N_{\text{el}} = \sum_{k>k_F,\sigma} \eta_{k\sigma}^* \eta_{k\sigma} \; , \quad N_{\text{holes}} = \sum_{k<k_F,\sigma} \eta_{k\sigma}^* \eta_{k\sigma} \; , \tag{3.167}$$

$$\mathcal{H} \equiv H_0 - \mu N = (E_0 - \mu N) + \sum_{k\sigma} \omega(k)\, \eta_{k\sigma}^* \eta_{k\sigma}, \tag{3.168}$$

where

$$\omega(k) = \begin{cases} \mu - k^2/2m & \text{if} \quad k < k_F, \\ k^2/2m - \mu & \text{if} \quad k > k_F, \end{cases} \tag{3.169}$$

so that $\omega(k) \geq 0$.

We would like to pay attention to a trick we made here: we introduced the new vacuum state, taking for it the previously found GS, and defined the *quasiparticle* creation and annihilation operators over this new vacuum state.

Fermi surface ...

density of states ...

Finally, when the electron gas interacts with an external potential $v(r)$ (e.g., due to an impurity in a metal), the perturbation is

$$H_{\text{int}} = \sum_{kk'\sigma} v_{kk'}\, c_{k\sigma}^* c_{k'\sigma} \; , \tag{3.170}$$

where

$$v_{kk'} = \langle k|v|k'\rangle = \frac{1}{V_{\text{vol}}} \int d^3r \; v(r)\, e^{-i(k-k')r} = \frac{1}{V_{\text{vol}}}\, v(k-k')\, . \tag{3.171}$$

In particular, for the Coulomb impurity we have

$$v(r) = e^2/r\, , \quad v(q) = 4\pi e^2/q^2. \tag{3.172}$$

3.10.6 Free (noninteracting) Bose gas

...

3.10.7 Noninteracting particles in an external field

...

3.10.8 Two-atomic molecule

Consider now a two-atomic molecule A–B. As the Hilbert space one might take the orbitals of one of the atoms, e.g., the atom A, because this basis is complete and, therefore, any state of the atom B may be expressed through the basis of the atom A. Clearly, however, that such a basis is inconvenient, especially for the symmetric molecule A–A. One might take, as the Hilbert space, the space $L = L_A \bigotimes L_B$, but this basis is overcomplete and may lead to wrong results. The solution of the problem is to use the orbitals of both atoms, but not the whole (infinite) sets of wavefunctions, but a reduced set, i.e. only a finite number n of them. Then for any $n < \infty$ the basis will be *incomplete* — it will never be overcomplete, and a larger is n, a more accurate will be the result.

For a qualitative description, it is already enough to take two orbitals, by one orbital from each atom. The Hamiltonian is:

$$H = \sum_\sigma \left[E_a n_{a\sigma} + E_b n_{b\sigma} + (V_{ab}\, c^*_{a\sigma} c_{b\sigma} + \text{h.c.})\right] . \tag{3.173}$$

Let us use the canonical transformation method, where we are looking for a solution in the form

$$\begin{aligned} c_{a\sigma} &= (1+\gamma^2)^{-1/2}(c_{1\sigma} + \gamma c_{2\sigma})\,, \\ c_{b\sigma} &= (1+\gamma^2)^{-1/2}(\gamma c_{1\sigma} - c_{2\sigma})\,, \end{aligned} \tag{3.174}$$

and we should choose γ so that to diagonalize the Hamiltonian, i.e. to reduce it to the form

$$H = \sum_\sigma (E_1 n_{1\sigma} + E_2 n_{2\sigma})\,. \tag{3.175}$$

The solution is:

$$\gamma = \sqrt{1 + \left(\frac{\Delta E}{2V}\right)^2} + \frac{\Delta E}{2V}\,, \tag{3.176}$$

$$E_{1,2} = \frac{E_a + E_b}{2} \pm \sqrt{\left(\frac{\Delta E}{2}\right)^2 + V^2}\,, \tag{3.177}$$

where

$$\Delta E = E_b - E_a\,, \quad V^2 = V_{ab} V_{ba}\,. \tag{3.178}$$

The Green functions are:

$$G^\sigma_{aa} = (\epsilon - E_b)/\mathcal{Z}\,, \quad G^\sigma_{ab} = V_{ab}/\mathcal{Z}\,, \tag{3.179}$$

where

$$\mathcal{Z} = (\epsilon - E_a)(\epsilon - E_b) - V^2 = (\epsilon - E_1)(\epsilon - E_2)\,. \tag{3.180}$$

The Green function may be rewritten as

$$G^\sigma_{aa} = \frac{\alpha_a}{\epsilon - E_1} + \frac{\beta_a}{\epsilon - E_2}\,, \tag{3.181}$$

where

$$\begin{aligned} \alpha_a &= \frac{E_b - E_1}{E_2 - E_1} = \frac{1}{2} + \frac{\Delta E}{4\sqrt{(\Delta E/2)^2 + V^2}}\,, \\ \beta_a &= \frac{E_2 - E_b}{E_2 - E_1} = \frac{1}{2} - \frac{\Delta E}{4\sqrt{(\Delta E/2)^2 + V^2}}\,, \end{aligned} \tag{3.182}$$

so that

$$\rho^\sigma_a(\epsilon) = \alpha_a \delta(E - E_1) + \beta_a \delta(E - E_2)\,. \tag{3.183}$$

Cases:
If $E_a = E_b$, we have $\gamma = 1$ and $E_{1,2} = E_a \pm |V|$.
If $E_a < E_b$, we have $\gamma > 1$ (?), and in the state $|1\rangle$, the electron disposition is closer to the atom A.

The Fermi level ϵ_F is determined from the equation

$$\sum_\sigma \int_{-\infty}^{\epsilon_F} d\epsilon \; [\rho_a^\sigma(\epsilon) + \rho_b^\sigma(\epsilon)] = N, \tag{3.184}$$

where N is the total number of electrons. If $N = 2$, then

$$\overline{n}_{a\sigma} = \alpha_a = \beta_b, \tag{3.185}$$

and the dissociation energy is equal to

$$D = (E_a - E_1) + (E_b - E_1). \tag{3.186}$$

`show fig!`

3.10.9 Gurney model

... virtual level, Friedel ocsillations ...

3.10.10 Two-body system

The Hamiltonian of two interacting particles,

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(Q_1, Q_2)\,, \tag{3.187}$$

may be rewritten as

$$H = \frac{P^2}{2M} + \frac{p^2}{2m} + V\,, \tag{3.188}$$

where the centre of mass variables are

$$P = P_1 + P_2\,, \tag{3.189}$$

$$Q = (m_1 Q_1 + m_2 Q_2)/M\,, \tag{3.190}$$

$$P = M\dot{Q}\,, \tag{3.191}$$

$$M = m_1 + m_2 \tag{3.192}$$

and the relative variables are

$$p = (m_2 p_1 - m_1 p_2)/M\,, \tag{3.193}$$

$$q = Q_1 - Q_2\,, \tag{3.194}$$

$$p = m\dot{q}\,, \tag{3.195}$$

$$m = m_1 m_2/M\,. \tag{3.196}$$

The relative kinetic energy may be rewritten as

$$p^2 = r^{-2} L^2 + p_r^2\,, \tag{3.197}$$

where L is the orbital momentum, $L = q \times p$, r is defined by

$$r^2 = q \cdot q\,, \tag{3.198}$$

and the radial momentum is introduced as

$$p_r = r^{-1}(q \cdot p - i\hbar)\,, \tag{3.199}$$

so that $p_r = m\dot{r}$.

Chapter 4

Approximate Methods

4.1 Adiabatic Approximation

When a system consists of particles of two types, light and heavy ones (e.g., electrons and nuclei), its dynamics may be considered within the *adiabatic approximation*, where light particles adiabatically follow the positions of heavy particles.

Let $\{r\}$ be the coordinates of light particles and $\{R\}$, the coordinates of heavy particles. Then, presenting the Hamiltonian as

$$H = H_0(r, R) + T_R \,, \tag{4.1}$$

where T_R is the kinetic energy of heavy particles, the eigenfunctions of the whole problem

$$H\Psi(r, R) = E\Psi(r, R) \tag{4.2}$$

may be looked for in a form

$$\Psi(r, R) = \sum_n \phi_n(R)\, \varphi_n(r, R), \tag{4.3}$$

where $\varphi_n(r, R)$ are eigenfunctions of the equation

$$H_0(r, R)\, \varphi_n(r, R) = \varepsilon_n(R)\, \varphi_n(r, R) \tag{4.4}$$

and R's are treated as the parameters. Thus, the problem (4.2) reduces to the equation

$$\{[T_R + \varepsilon_n(R)] - E\}\, \phi_n(R) \approx 0 \,. \tag{4.5}$$

4.2 Thomas–Fermi Approximation

For a nonrelativistic Fermi system of charged particles (e.g., for the electron gas) the potential energy may be written as

$$V(r) = e\varphi(r) \,, \tag{4.6}$$

where e is the charge and $\varphi(r)$ is the potential which satisfies the Poisson equation

$$\nabla^2 \varphi(r) = 4\pi e n(r) \,, \tag{4.7}$$

$n(r)$ being the density of particles. When (*i*) the potential varies slowly, and (*ii*) the particles move slowly (a quasi-adiabatic case), we may put approximately

$$n(r) = 2(\text{spin}) \frac{1}{(2\pi)^3} \frac{4}{3} \pi k_F^3(r) \,, \quad \frac{\hbar^2 k_F^2(r)}{2m} = \mu - e\varphi(r) \tag{4.8}$$

assuming that the chemical potential μ is constant (i.e., it is the same for the whole system) and is determined by the total number of particles. The coupled system of equations (4.7, 4.8) corresponds to the *Thomas-Fermi* (TF) approximation.

In the *linearized* TF approximation we also put (+ or − ?)

$$n(r) = \frac{1}{3\pi^2}\left[\frac{2m}{\hbar^2}\left(\mu + e\varphi(r)\right)\right]^{3/2} \approx n + \frac{3}{2}\frac{n}{\epsilon_F}e\varphi(r)\,. \tag{4.9}$$

The Poisson equation then reduces to

$$\nabla^2\varphi(r) = k_{\mathrm{TF}}^2\varphi(r)\,, \tag{4.10}$$

which leads to a screening, $\varphi(r) \propto e^{-k_{\mathrm{TF}}r}$, with the TF momentum

$$k_{\mathrm{TF}}^2 = \frac{6\pi n e^2}{\epsilon_F} = \frac{2.6}{r_s}\ \text{a.u.} \tag{4.11}$$

4.3 Method of Motion Equations

Let one can find an operator A such that it satisfies the equation

$$[H, A^*]_-|\Psi_0\rangle = \hbar\omega A^*|\Psi_0\rangle\,, \tag{4.12}$$

then the operator A^* creates an excitation with the energy $\hbar\omega$.

Proof: the state $A|\Psi_0\rangle$ has the energy $E_0 - \hbar\omega$,

$$HA|\Psi_0\rangle = (E_0 - \hbar\omega)A|\Psi_0\rangle\,. \tag{4.13}$$

But because E_0 is the minimum energy of the system, it must be $A|\Psi_0\rangle = 0$, i.e. A is the annihilation operator, therefore A^* should be the corresponding creation operator,

$$HA^*|\Psi_0\rangle = (E_0 + \hbar\omega)A^*|\Psi_0\rangle\,. \tag{4.14}$$

If we can find an operator A such that it satisfies the *operator* equation

$$[H, A^*]_- = \hbar\omega A^*, \tag{4.15}$$

then this system has a Bosonic (equidistant) spectrum, i.e. the state $(A^*)^2|\Psi_0\rangle$ has the energy $2\hbar\omega$, the state $(A^*)^3|\Psi_0\rangle$ has the energy $3\hbar\omega$, *etc.*

In a general case, we have to find a set of operators $\{A_j^*\}$ which satisfy the equations

$$[H, A_j^*]_- = \hbar\omega_j A_j^*\,, \tag{4.16}$$

then the creation operator A_j^* creates its own type of excitation.

If we have found a closed set of operators $\{A_n\}$ such that

$$[A_n, H]_- = \sum_m K_{nm}A_m\,, \tag{4.17}$$

then, using the equation

$$\langle[[A_n, H]_-, A_l^*]_\eta\rangle = \sum_m K_{nm}\langle[A_m, A_l^*]_\eta\rangle\,, \tag{4.18}$$

we can calculate the corresponding Green functions,

$$\langle\langle A_n, B\rangle\rangle_\omega = \sum_m \left((\omega - \mathbf{K})^{-1}\right)_{nm}\langle[A_m, B]_\eta\rangle\,. \tag{4.19}$$

4.4 WKB Approximation

Looking for a solution of the Schrödinger equation in the quasi-classical approximation, let us substitute the wavefunction

$$\psi(r,t) = \exp\left[\frac{i}{\hbar}S(r,t)\right] \tag{4.20}$$

into the Schrödinger equation thus obtaining the equation for the function $S(r,t)$,

$$\frac{\partial S}{\partial t} = -\frac{(\nabla S)^2}{2m} - V(r) + \frac{i\hbar}{2m}\nabla^2 S\,. \tag{4.21}$$

If $(\nabla S)^2 \gg \hbar(\nabla^2 S)$, or

$$p^2 \gg \hbar\frac{\partial p}{\partial x} = \frac{m\hbar}{p}\left|\frac{\partial V}{\partial x}\right|, \tag{4.22}$$

the last term in the r.h.s. of Eq. (4.21) may be neglected, and it reduces to the classical Hamilton-Yacobi equation, $S(r,t)$ being the *action*.

In the *stationary state*, when $\psi(r,t) = e^{-iEt/\hbar}\varphi(r)$, the action takes the form $S(r,t) = \sigma(r) - Et$, where the function $\sigma(r)$ satisfies the equation

$$\frac{(\nabla\sigma)^2}{2m} + V(r) - \frac{i\hbar}{2m}\nabla^2\sigma = E\,. \tag{4.23}$$

Looking for a solution of this equation in a series of $\hbar$,

$$\sigma(r) = \sigma_0(r) + \left(\frac{\hbar}{i}\right)\sigma_1(r) + \left(\frac{\hbar}{i}\right)^2\frac{1}{2!}\sigma_2(r) + \ldots, \tag{4.24}$$

we obtain in the lowest ($\hbar^0$) order

$$\frac{(\nabla\sigma_0)^2}{2m} + V(r) = E\,. \tag{4.25}$$

In the one-dimensional case this equation has the solution

$$\sigma_0(x) = \pm\int_a^x dx\, p(x)\,, \quad p(x) = \sqrt{2m[E - V(x)]}\,, \tag{4.26}$$

or

$$\varphi(x) = \frac{C_1}{|p(x)|}\exp\left(\frac{i}{\hbar}\int_a^x dx\, p(x)\right) + \frac{C_2}{|p(x)|}\exp\left(-\frac{i}{\hbar}\int_a^x dx\, p(x)\right) \tag{4.27}$$

$$= \frac{C}{|p(x)|}\sin\left(\alpha + \frac{1}{\hbar}\int_a^x dx\, p(x)\right). \tag{4.28}$$

The WKB (Wentzel–Kramers–Brillouin) approximation is rigorous when $|p(x)|$ is large, i.e. when $E \neq V(x)$. When $E < V(x)$, then $p(x)$ is complex, and Eq. (8.14) describes the tunnelling effect.

The next order in $\hbar$ leads to the equation

$$\nabla\sigma_1 = \frac{\nabla^2\sigma_0}{2\nabla\sigma_0}\,, \tag{4.29}$$

which gives

$$\sigma_1(x) = \text{const} + \ln\left[p(x)\right]^{-1/2}. \tag{4.30}$$

4.5 Conventional Perturbation Theory

For the Hamiltonian

$$H = H_0 + gV, \tag{4.31}$$

where H_0 has the eigenvectors $|\varphi_n\rangle$,

$$H_0|\varphi_n\rangle = E_m|\varphi_n\rangle, \tag{4.32}$$

the eigenfunctions of H may be looked for in the form

$$|\psi\rangle = \sum_n a_n\,|\varphi_n\rangle. \tag{4.33}$$

This leads to the eigenvalue problem

$$(E - E_m)\,a_m = g\sum_n a_n V_{mn}\,, \tag{4.34}$$

or

$$\text{Det}\,\left[(E_m - E)\,\delta_{mn} + gV_{mn}\right] = 0\,. \tag{4.35}$$

Solving this problem by iterations, we obtain

$$\psi_{(l)} = \varphi_l + g\sum_{n\neq l}\frac{V_{nl}}{E_l - E_n}\varphi_n + \ldots \tag{4.36}$$

and

$$E_{(l)} = E_l + gV_{ll} + g^2\sum_{n\neq l}\frac{|V_{nl}|^2}{E_l - E_n} + \ldots \tag{4.37}$$

When two levels of H_0 are degenerated, say $E_1 \approx E_2$, first we have to solve exactly the eigenvalue problem for the two levels 1 and 2 thus finding the new energies E_1' and E_2' and wavefunctions φ_1' and φ_2', and then use the basis with these two new states instead the old ones; then the divergence disappears.

4.6 Stationary Perturbation Theory

Let us introduce the wavefunctions $|\Upsilon_n\rangle = C|\Psi_n\rangle$, where the constant C is chosen so that $\langle\Phi_n|\Upsilon_n\rangle = 1$. Then

$$\Delta E = \langle\Phi_0|V|\Upsilon_0\rangle\,. \tag{4.38}$$

Introduce also the projection operator

$$Q = 1 - |\Phi_0\rangle\langle\Phi_0| \tag{4.39}$$

and suppose that the ground state $|\Phi_0\rangle$ is nondegenerated. Then one can easily find that

$$(u - H_0)|\Upsilon_0\rangle = (u - H + V)|\Upsilon_0\rangle = (u - E_0^{\text{exact}} + V)|\Upsilon_0\rangle \tag{4.40}$$

and

$$|\Upsilon_0\rangle = |\Phi_0\rangle + Q|\Upsilon_0\rangle = |\Phi_0\rangle + \frac{Q}{u - H_0}(u - E_0^{\text{exact}} + V)|\Upsilon_0\rangle\,, \tag{4.41}$$

where u is a parameter. Equations (4.41) may be solved by iterations, leading to the series

$$|\Upsilon_0\rangle = \sum_{n=0}^{\infty} \left[\frac{Q}{u-H_0}(u - E_0^{\text{exact}} + V)\right]^n |\Phi_0\rangle\,. \tag{4.42}$$

The choice $u = E_0^{\text{exact}}$ leads to the *Brillouin–Wigner* perturbation series,

$$|\Upsilon_0\rangle = |\Phi_0\rangle + \frac{1}{E_0^{\text{exact}} - H_0} QV|\Phi_0\rangle + \frac{1}{E_0^{\text{exact}} - H_0} QV \frac{1}{E_0^{\text{exact}} - H_0} QV|\Phi_0\rangle + \dots \tag{4.43}$$

and

$$\Delta E = \langle\Phi_0|V|\Phi_0\rangle + \langle\Phi_0|V\frac{Q}{E_0^{\text{exact}} - H_0}V|\Phi_0\rangle + \langle\Phi_0|V\frac{Q}{E_0^{\text{exact}} - H_0}V\frac{Q}{E_0^{\text{exact}} - H_0}V|\Phi_0\rangle + \dots \tag{4.44}$$

The choice $u = E_0$ results in the *Rayleigh–Schrödinger* perturbation series,

$$\begin{aligned}\Delta E = \langle\Phi_0|V|\Phi_0\rangle &+ \langle\Phi_0|V\frac{Q}{E_0 - H_0}V|\Phi_0\rangle + \langle\Phi_0|V\frac{Q}{E_0 - H_0}V\frac{Q}{E_0 - H_0}V|\Phi_0\rangle \\ &- \langle\Phi_0|V|\Phi_0\rangle\langle\Phi_0|V\frac{Q}{(E_0 - H_0)^2}V|\Phi_0\rangle + \dots\end{aligned} \tag{4.45}$$

This variant of the perturbation theory operates for many-body systems, because “incorrect” terms are cancelled with unconnected diagrams of the “correct” terms.

4.7 Dynamic Perturbation Theory

Let

$$H = H_0 + g(t)\,V\,, \tag{4.46}$$

where $g(t) = 0$ at $t \to -\infty$ and $g(0) = 1$, for example,

$$g(t) = g e^{-\delta|t|}\,, \tag{4.47}$$

where $\delta \to 0$, and in the final expressions we have to put $g = 1$. Equation (4.47) corresponds to adiabatically slow turning on of the interaction.

Introduce the *adiabatic operator* S as

$$S(t,t_0) = e^{iH_0t}\,U(t,t_0)\,e^{-iH_0t}\,. \tag{4.48}$$

$S(t,t_0)$ is the unitary operator, and it satisfies the equation

$$i\hbar\frac{\partial}{\partial t}S(t,t_0) = g(t)\,V(t)\,S(t,t_0)\,, \quad S(t,t_0)|_{t=t_0} = 1\,, \tag{4.49}$$

where $V(t) = e^{iH_0t}\,Ve^{-iH_0t}$. The adiabatic operator may be considered as the evolution operator in the interaction representation, $|\psi(t)\rangle_{\text{int}} = S(t,t_0)|\psi(t_0)\rangle_{\text{int}}$.

A formal solution of Eq. (4.49) is

$$S(t,t_0) = 1 - i\int_{t_0}^{t} dt_1\, g(t_1)V(t_1)S(t_1,t_0)\,. \tag{4.50}$$

Iterating this equation, we obtain the perturbation series

$$S(t,t_0) = \sum_{n=0}^{\infty}(-i)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \ldots \int_{t_0}^{t_{n-1}} dt_n \, g(t_1)g(t_2)\ldots g(t_n)\, V(t_1)V(t_2)\ldots V(t_n)\,. \tag{4.51}$$

Using the chronological operator $P_{\rm ch}$, this series may be rewritten as

$$S(t,t_0) = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \, g(t_1)g(t_2)\ldots g(t_n)\, P_{\rm ch}[V(t_1)V(t_2)\ldots V(t_n)]\,. \tag{4.52}$$

Substituting Eq. (4.47) into Eq. (4.52), we obtain

$$S_\delta \equiv S(0,-\infty) = \sum_{n=0}^{\infty}(-i)^n \frac{g^n}{n!} \int_{-\infty}^{0} dt_1 \int_{-\infty}^{0} dt_2 \ldots \int_{-\infty}^{0} dt_n \, e^{\delta(t_1+t_2+\ldots+t_n)}\, P_{\rm ch}[V(t_1)V(t_2)\ldots V(t_n)]\,. \tag{4.53}$$

One can check that the operator S_δ satisfies the following identity (Gell-Mann and Chow),

$$[H_0, S_\delta]_- = -gVS_\delta + i\hbar\delta g \frac{\partial}{\partial g} S_\delta\,. \tag{4.54}$$

Then, after some algebra described in detail in a number of textbooks (which all reduce to the proof that the adiabatic hypothesis is rigorous here) one can obtain finally

$$|\Psi_n(g)\rangle = \lim_{\delta\to+0}\frac{S_\delta|\Phi_n\rangle}{\langle\Phi_n|S_\delta|\Phi_n\rangle} \tag{4.55}$$

and

$$\Delta E_n(g) = \lim_{\delta\to+0} i\hbar\delta g \frac{\partial}{\partial g} \ln\langle\Phi_n|S_\delta|\Phi_n\rangle\,. \tag{4.56}$$

In the case of degenerated spectrum, these equations coincide with the Rayleigh–Schrödinger perturbation series.

The described dynamic perturbation theory forms the base for the diagram perturbation theory described below in Sec. 8.14.

Chapter 5

Linear Response Theory

The linear response technique is one of the most powerful methods used in solid state physics.

First, the linear response describes most experiments. Namely, let a coherent flux of particles (e.g., photons, electrons, protons, neutrons, ions, atoms, or even molecules) with a given energy ε_{ini} and momentum $p_{\text{ini}} = \hbar k_{\text{ini}}$ (and, may be, with given values of internal degrees of freedom such as spin) be directed to a target (one atom or molecule, gas, liquid, amorphous or crystalline solid), and then the scattered flux is analyzed, i.e., the intensity of the scattered flux with a given energy ε_{fin} and momentum $p_{\text{fin}} = \hbar k_{\text{fin}}$ (and, may be, spin) is measured. Such experiments give in principle the whole information about the object, namely its geometrical structure (*diffraction* experiments – the main point in this approach is to analyze the angle distribution of scattered particles) and its internal structure (*inelastic spectroscopy* experiments), i.e. the dispersion of excitations (low-energy excitations, which are usually treated as quasiparticles – phonons, electron-hole pairs, excitons, plasmons, magnons, *etc.*, and high-energy excitations such as electronic transitions between different levels, or atomic displacements such as creation of defects or even evaporation of atoms from a target surface). It is clear, however, that so rich information cannot be extracted without a theoretical support – we have to compare the experimental cross-section scattering intensities with those predicted by theory.

Second, the linear response theory and the generalized susceptibility calculated within its framework, gives in principle all information about the given state (which may be nonequilibrium in a general case) of the system under consideration. Besides, it describes also the scattering experiments *when the interaction of the particle with the target may be considered as a "weak" perturbation*. Namely, this is correct for light scattering, diffraction of high-energy electrons, scattering of atoms with thermal energies, but not so for laser, X-ray and gamma scattering, LEED, SIMS; in the later cases a more accurate description should be used.

The cross-section of scattering is connected with the corresponding correlation function depending on the type of particles and the mechanism of their interaction with the target. In turn, the correlation function is coupled with the corresponding generalized susceptibility. Generalized susceptibilities may be of different types; recall $\epsilon(k, \omega)$ simplest.

5.1 Scattering Theory

In general, the problem reduces to writing the Hamiltonian in a form

$$H = H_{\text{particle}} + H_{\text{target}} + H_{\text{int}} \tag{5.1}$$

and then to solution of the Schrödinger equation $i\hbar\dot{\Psi} = H\Psi$ with given initial conditions. As the initial state it is natural to take the plane wave

$$|\Psi_{\rm ini}\rangle = \frac{1}{\sqrt{V_{\rm vol}}} e^{ik_{\rm ini}x - i\omega_{\rm ini}t} |\sigma_{\rm ini}\rangle\,, \tag{5.2}$$

where $|\sigma_{\rm ini}\rangle$ describes internal degrees of freedom of the incoming particle such as spin of the incoming electron or a state of the incoming atom, and also includes the description of the initial state of the target. The state (5.2) corresponds to the flux of particles which is equal to

$$j_{\rm ini} = \frac{\hbar}{2m_{\rm ini}i}\left(\Psi^*_{\rm ini}\,\nabla\Psi_{\rm ini} - \Psi_{\rm ini}\,\nabla\Psi^*_{\rm ini}\right) = \frac{\hbar k_{\rm ini}}{m_{\rm ini}V_{\rm vol}} = \frac{p_{\rm ini}}{m_{\rm ini}V_{\rm vol}} = \frac{v_{\rm ini}}{V_{\rm vol}}\,. \tag{5.3}$$

However, usually it is simpler to assume that the incoming flux is constant, and to consider the *stationary* Schrödinger equation, looking for its solution in a form

$$\Psi = \Psi_{\rm ini} + \delta\Psi^+ \tag{5.4}$$

with the special *boundary* conditions corresponding to *outgoing* (scattered) waves in Ψ^+. Then, the intensity of the scattered flux with given parameters is proportional to $|\langle\Psi|\Psi_{\rm fin}\rangle|^2$, where

$$|\Psi_{\rm fin}\rangle = \frac{1}{\sqrt{V_{\rm vol}}} e^{ik_{\rm fin}x - i\omega_{\rm fin}t} |\sigma_{\rm fin}\rangle\,. \tag{5.5}$$

The *differential scattering cross-section* is then defined by

$$\frac{d^2\sigma}{d\varepsilon\, d\Omega} = \frac{|j_{\rm fin}|}{|j_{\rm ini}|}\,, \tag{5.6}$$

where $j_{\rm fin}\, d\varepsilon\, d\Omega$ is a part of the flux of particles scattered in the direction $k_{\rm fin}$ in the solid angle $d\Omega$ with the energies $\varepsilon_{\rm fin} < \varepsilon < \varepsilon_{\rm fin} + d\varepsilon$. Taking into account the normalization (8.14), the cross-section is determined by

$$\frac{d^2\sigma}{d\varepsilon\, d\Omega} = |B|^2 \frac{m_{\rm ini}|k_{\rm fin}|}{m_{\rm fin}|k_{\rm ini}|}\,, \tag{5.7}$$

where

$$B(q,\omega) = \langle\Psi_{\rm fin}|\delta\Psi^+\rangle \tag{5.8}$$

and

$$q = k_{\rm ini} - k_{\rm fin}\,, \tag{5.9}$$

$$\hbar\omega = \varepsilon_{\rm ini} - \varepsilon_{\rm fin}\,. \tag{5.10}$$

Note that the energy and momentum are not independent parameters, they are coupled by the relation $\varepsilon_{\rm ini} = p^2_{\rm ini}/2m_{\rm ini}$ for the nonrelativistic particles with nonzero rest mass (e.g., electrons), or by the relation $\varepsilon_{\rm ini} \equiv \hbar\omega_{\rm ini} = \hbar c|k_{\rm ini}|$ for photons (light scattering experiments), and similar relations for the scattered particles in the final state. Therefore, as independent parameters, the energy and two angles are chosen usually.

Until this point the described approach is exact. In the linear response theory, however, the interaction of the external flux with the system is assumed to be weak, and the scattering probability $B(q,\omega)$ is calculated in the Born approximation (i.e., in the first order of the perturbation theory), so that it is given by the *Fermi golden rule*:

$$|B(q,\omega)|^2 = \frac{2\pi}{\hbar}|\langle\Psi_{\rm fin}|H_{\rm int}|\Psi_{\rm ini}\rangle|^2\delta(\varepsilon_{\rm fin} + \hbar\omega - \varepsilon_{\rm ini})\,. \tag{5.11}$$

The Born approximation is accurate in two limiting cases. If we denote by U the amplitude of the interaction H_{int} and by R its effective radius, then the first limit corresponds to a weak interaction, $U \ll \hbar^2/m_{\text{ini}}R^2$, and the second limit corresponds to fast particles, $U \ll \left(\hbar^2/m_{\text{ini}}R^2\right) k_{\text{ini}}R$, when the interaction time is short. The scattering in the Born approximation is additive, i.e. it corresponds to *kinematic* diffraction (multiple-scattering events are neglected). Notice that the optical theorem (the conservation of probabilities) does not operate in this approximation.

As an example, let us consider the case when the interaction Hamiltonian may be presented in the form

$$H_{\text{int}}(r) = \sum_a v_{\text{at}}(r - r_a) = \int dr' \, \rho(r') \, v_{\text{at}}(r - r') \,, \tag{5.12}$$

where r is the coordinate of the external particle, and

$$\rho(r') = \sum_a \delta(r' - r_a) \tag{5.13}$$

is the local density of target atoms interacting with the incoming flux. When the system is characterised by a hierarchy of times as, e.g., in the adiabatic approximation where electronic processes are much faster then the motion of atoms, so that the target wavefunction may be presented as $|\sigma\rangle = |\sigma^{(\text{at})}\rangle|\sigma^{(\text{el})}\rangle$, then the matrix element in (5.11) may be split into two factors,

$$\langle \Psi_{\text{fin}}|H_{\text{int}}|\Psi_{\text{ini}}\rangle = S(q\omega_1) \, V(q\omega_2) \,, \tag{5.14}$$

where $\omega_1 + \omega_2 = \omega$, $V(q\omega)$ is the *atomic form-factor*,

$$V(q\omega) = \int dr' \, e^{-iqr'} \langle \sigma_{\text{fin}}^{(\text{el})}| \, v_{\text{at}}(r') \, |\sigma_{\text{ini}}^{(\text{el})}\rangle \,, \tag{5.15}$$

and $S(q\omega)$ is the so-called (dynamic) *structure form-factor*,

$$S(q) = \frac{1}{V_{\text{vol}}} \int dr' \, e^{-iqr'} \langle \sigma_{\text{fin}}^{(\text{el})}|\rho(r')|\sigma_{\text{ini}}^{(\text{el})}\rangle \,. \tag{5.16}$$

Such a splitting is rigorous if either $|\omega_1| \ll |\omega_2|$ or $|\omega_1| \gg |\omega_2|$. For the sake of simplicity we assume in what follows that $\omega_2 = 0$.

Now, presenting the delta-function in (5.11) in the integral form,

$$\delta(\varepsilon_{\text{fin}} - \varepsilon_{\text{ini}} - \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \, e^{i\omega t} e^{iE_{\text{ini}}t/\hbar} e^{-iE_{\text{fin}}t/\hbar}, \tag{5.17}$$

we may rewrite the matrix element (5.11) in the form

$$\begin{aligned} |B(q\omega)|^2 &= \frac{2\pi}{\hbar}\frac{1}{2\pi\hbar}\frac{|V(q)|^2}{V_{\text{vol}}^2} \iint dr' \, dr'' \, e^{iqr' - iqr''} \int_{-\infty}^{+\infty} dt \, e^{i\omega t} e^{iE_{\text{ini}}t/\hbar} \\ &\qquad \times \langle \sigma_{\text{ini}}|\rho(r')|\sigma_{\text{fin}}\rangle e^{-iE_{\text{fin}}t/\hbar} \langle \sigma_{\text{fin}}|\rho(r'')|\sigma_{\text{ini}}\rangle \\ &= \frac{|V(q)|^2}{\hbar^2 V_{\text{vol}}^2} \iint dr' \, dr'' \, e^{iq(r' - r'')} \int_{-\infty}^{+\infty} dt \, e^{i\omega t} \langle \sigma_{\text{ini}}|\rho(r', t)\rho(r'', 0)|\sigma_{\text{ini}}\rangle \,, \end{aligned} \tag{5.18}$$

where at the last step we took into account that in scattering experiments the final state of the target is not defined and, therefore, we have to sum over all possible intermediate states of the target. Then, after averaging over the final states of the particle (?!!),

$$\sum_f \to \frac{d^3k_f}{(2\pi)^3} = k_f^2 \, dk_f \, d\Omega_f = \left(\frac{m}{\hbar}\right)^2 k_f \, d\varepsilon_f \, d\Omega_f \,, \tag{5.19}$$

the cross-section finally takes the form

$$\frac{d^2\sigma}{d\varepsilon\, d\Omega} = V_{\text{vol}} \frac{k_{\text{fin}}}{k_{\text{ini}}} \frac{1}{(2\pi)^3} \frac{m_{\text{fin}}^2}{\hbar^5} |V(q)|^2 \left[Q_{\text{elastic}}(q)\delta(\omega) + Q_{\rho\rho}(q\omega) \right]. \tag{5.20}$$

The first term in square brackets describes the elastic scattering on target atoms with fixed positions, and the second one is the correlation function

$$Q_{\rho\rho}(q\omega) = \iint dr'\, dr''\, e^{iq(r'-r'')} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle \delta\rho(r',t)\, \delta\rho(r'',0) \rangle \tag{5.21}$$

for the density fluctuations,

$$\delta\rho(r) = \rho(r) - \langle \rho(r) \rangle . \tag{5.22}$$

Equation (5.20) is the desired expression which couples the cross-section of inelastic scattering with the correlation function.

Let us consider the scattering when the target corresponds to an ideal crystal, so that the atomic coordinates are

$$r_l = l + u_l\,, \quad u_l = \sum_q u_q e^{iql} + \text{h.c.} \tag{5.23}$$

In this case the structure form-factor may be presented as

$$\begin{aligned} S(K) \equiv \frac{1}{V_{\text{vol}}} \sum_l e^{-iKr_l} &= \frac{1}{V_{\text{vol}}} \sum_l \exp\left\{ -iK \left[l + \sum_q \left(u_q e^{iql} + \text{h.c.} \right) \right] \right\} \\ &= \frac{1}{V_{\text{vol}}} \sum_l e^{-iKl} \prod_q \exp\left(-iKu_q e^{iql} + \text{h.c.} \right) \\ &\approx \frac{1}{V_{\text{vol}}} \sum_l e^{-iKl} \prod_q \left[1 - iK \left(u_q e^{iql} + \text{h.c.} \right) - \frac{1}{2} |Ku_q|^2 \right] \\ &= \left[S^{(0)}(K) + S^{(1)}(K) + \ldots \right] e^{-W}. \end{aligned} \tag{5.24}$$

Here $S^{(0)}(K)$ describes the classical (Bragg's) elastic diffraction,

$$S^{(0)}(K) = \frac{1}{\Omega\_0} \delta_{K,g}\,, \tag{5.25}$$

where g is a vector of the inverse lattice. In diffraction, the elastic scattering with $K = g \neq 0$ is possible because this momentum is taken away by the lattice as a whole; because the total mass M_{lattice} of the lattice is infinite, the corresponding energy $\hbar^2 g^2 / 2M_{\text{lattice}}$ is zero.

The term $S^{(1)}(K)$ corresponds to one-phonon processes,

$$S^{(1)}(K) = \frac{1}{\Omega_0} \sum_q (-iKu_q)\, \delta_{K,g+q}\,, \tag{5.26}$$

where also the energy conservation law should be taken into account. The processes with $g = 0$ are called the normal (N-) processes, and those with $g \neq 0$ are called the Umklapp (U-) processes.

Finally, the factor e^{-W} is the *Debye-Waller factor*. It gives the main contribution coming from multiphonon processes and leads to the decreasing of the scattered intensity, $I = I_0 e^{-2W}$. The Debye-Waller factor is defined as

$$e^{-W} = \prod_q \left[1 - \frac{1}{2} |Ku_q|^2 \right] = \exp\left(-\sum_q \frac{1}{2} |Ku_q|^2 \right). \tag{5.27}$$

Assuming that $|Ku_q|^2 \approx \frac{1}{3}K^2|u_q|^2$ and using the Debye model, the Debye-Waller factor is equal to

$$W = \frac{3}{2}\frac{\hbar^2 K^2 T^2}{m k_B \Theta_D^2}\int_0^{\Theta_D/T} dz\, z\left(\frac{1}{e^z-1}+\frac{1}{2}\right) \approx \begin{cases} \frac{3}{2}\frac{\hbar^2 K^2 T}{m k_B \Theta_D^2} & \text{if} \quad T\to\infty\,, \\ \frac{3}{8}\frac{\hbar^2 K^2}{m k_B \Theta_D} & \text{if} \quad T \to 0\,, \end{cases} \tag{5.28}$$

the $T \to 0$ case describes the contribution of zero vibrations.

`! Connection with previous ?! DW is missing ?`

5.2 Correlation Functions

The *correlation function* for two operators $A(t)$ and $B(t)$ (in Heisenberg representation) is *defined* as

$$Q_{AB}(t) = \langle \delta A(0)\, \delta B(t)\rangle\,, \tag{5.29}$$

where

$$\delta A(t) = A(t) - \langle A(t)\rangle\,. \tag{5.30}$$

Theorem:

$$Q_{AB}(-t) = Q_{BA}(t+i\beta\hbar) = \exp\left(i\beta\hbar\frac{\partial}{\partial t}\right) Q_{BA}(t)\,, \tag{5.31}$$

or

$$\widehat{Q}_{AB}(-\omega_R) = e^{-\beta\hbar\omega_R}\widehat{Q}_{BA}(\omega_R)\,. \tag{5.32}$$

Proof:

$$\begin{aligned} Q_{AB}(t) &\propto \text{Sp}\left[e^{-\beta H}A(0)B(t)\right] = \text{Sp}\left[A(0)\left(e^{-\beta H}e^{+\beta H}\right)B(t)e^{-\beta H}\right] \\ &= \text{Sp}\left[A(0)e^{-\beta H}B(t-i\beta\hbar)\right] = \text{Sp}\left[e^{-\beta H}B(t-i\beta\hbar)A(0)\right] \\ &= \text{Sp}\left[B(0)A(-t+i\beta\hbar)\right] \propto Q_{BA}(-t+i\beta\hbar)\,. \end{aligned} \tag{5.33}$$

Consequence: if $T=0$, then $\widehat{Q}(\omega_R)=0$ for $\omega_R<0$.
Note: in the classical mechanics case, we have to take the limit $\hbar \to 0$.

5.3 Generalized Susceptibility

Let the interaction has the form

$$H_{\text{int}} = -\widehat{x}f(t)\,, \tag{5.34}$$

where $f(t)$ is the (infinitesimal) external force (perturbation), and $\widehat{x}$ is an operator of the system under consideration. In a general case Eq. (5.34) should be rewritten as

$$H_{\text{int}} = -\frac{1}{2}\left[\widehat{\mathbf{x}}\mathbf{f}(t) + \text{h.c.}\right] = -\frac{1}{2}\sum_k\left[\widehat{x}_k f_k(t) + \text{h.c.}\right]\,. \tag{5.35}$$

The *linear response* is

$$\langle x(t)\rangle = \int_0^\infty d\tau\, \alpha(\tau)\, f(t-\tau)\,. \tag{5.36}$$

Equation (5.36) is the *definition* of the *generalized susceptibility* α.

As usual, the Fourier transform is defined by

$$\langle x(\omega)\rangle = \alpha(\omega)\, f(\omega)\,, \tag{5.37}$$

where

$$\alpha(\omega)=\alpha_R(\omega)+i\alpha_I(\omega)=\int_0^\infty dt\,\alpha(t)\,e^{+i\omega t}. \tag{5.38}$$

Define also

$$\omega=\omega_R+i\omega_I\,. \tag{5.39}$$

Owing two conditions,
(1) $\alpha(t)$ is real, and
(2) causality (the lower limit in Eqs. (5.36, 5.38) is zero),
we have according to general results of Sec. 2.5.1 the following consequences:

1. Directly from the definition it follows that $\alpha(\omega)=\alpha^*(-\omega)$. Therefore, $\alpha_R(\omega)$ is the even function, while $\alpha_I(\omega)$ is the odd function.

2. From the definition and causality it follows that $\alpha(\omega)$ is an analytical function on the upper half-plane, including the real axis (except, may be, the point $\omega_R=0$).

3. From the definition it follows that $\alpha(-\omega^*)=\alpha^*(\omega)$. Therefore, $\alpha(i\omega_I)$ is real.

4. *Theorem*:
in the upper half-plane, $\alpha(\omega)$ takes real values *only* on the imaginary axis;
$\alpha(i\omega_I)$ monotonically decreases when ω_I increases, and $\alpha(i\infty)=0$.

Therefore, $\alpha(\omega)$ has no zeroes in the upper half-plane (for proof see Landau V p.414).

5. H. A. Kramers and R. L. Kronig relations (dispersion relations):

$$\alpha_R(\omega)=\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{+\infty}d\omega_1\,\frac{\alpha_I(\omega_1)}{\omega_1-\omega}=\frac{2}{\pi}\mathcal{P}\int_0^{+\infty}d\omega_1\,\frac{\omega_1\,\alpha_I(\omega_1)}{\omega_1^2-\omega^2}\,, \tag{5.40}$$

$$\alpha_I(\omega)=-\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{+\infty}d\omega_1\,\frac{\alpha_R(\omega_1)}{\omega_1-\omega}+\left(\frac{A}{\omega}\quad\text{if}\quad\alpha(\omega\sim 0)\approx i\frac{A}{\omega}\right)\,. \tag{5.41}$$

(Proof is trivial, e.g. see Sec. 2.5.1 or Landau V p.416).

6. Therefore,

$$\alpha(i\omega)=\frac{2}{\pi}\int_0^{+\infty}d\omega_1\,\frac{\omega_1\,\alpha_I(\omega_1)}{\omega_1^2+\omega^2}\quad\text{and}\quad\int_0^{+\infty}d\omega\,\alpha(i\omega)=\int_0^{+\infty}d\omega\,\alpha_I(\omega). \tag{5.42}$$

7. R. Kubo (1956): $\alpha(\omega)$ may be calculated by

$$\alpha_{ik}(\omega)=\frac{i}{\hbar}\int_0^\infty dt\,e^{i\omega t}\Big\langle\widehat{x}_i(t)\,\widehat{x}_k^*(0)-\widehat{x}_k^*(0)\,\widehat{x}_i(t)\Big\rangle, \tag{5.43}$$

or

$$\operatorname{Im}\widehat{\alpha}_{ik}(\omega_R)=\left[\frac{1}{2\hbar}\tanh\left(\frac{\hbar\omega_R}{2k_BT}\right)\right]\int_{-\infty}^{+\infty}dt\,e^{i\omega_R t}\Big\langle\widehat{x}_i(t)\,\widehat{x}_k^*(0)+\widehat{x}_k^*(0)\,\widehat{x}_i(t)\Big\rangle. \tag{5.44}$$

In the classical mechanics limit we have to put

$$\frac{1}{i\hbar}(AB-BA)\to\sum_a\left(\frac{\partial A}{\partial r_a}\frac{\partial B}{\partial p_a}-\frac{\partial A}{\partial p_a}\frac{\partial B}{\partial r_a}\right) \tag{5.45}$$

and

$$\left[\frac{1}{2\hbar}\tanh\left(\frac{\hbar\omega_R}{2k_BT}\right)\right]\to\frac{\omega_R}{4k_BT}\,. \tag{5.46}$$

The proof may be found in a number of textbooks, e.g. see Landau V p.428. Here we outline the main steps only:
(1) use an adiabatically slow increasing force, $f(t)\propto e^{\delta t}$;

(2) use the standard perturbation theory: $H_0|n^{(0)}\rangle = E_n|n^{(0)}\rangle$, where $|n^{(0)}(t)\rangle = e^{-iE_nt}|n^{(0)}\rangle$;
(3) for the equation $i\hbar\frac{\partial}{\partial t}|n(t)\rangle = [H_0 + H_{\rm int}(t)]|n(t)\rangle$, look for its solution in the form $|n(t)\rangle = |n^{(0)}(t)\rangle + \sum_m a_{nm}(t)\,|m^{(0)}(t)\rangle$;
(4) the first-order solution is

$$a_{mn}(t) \approx -\frac{1}{2i\hbar}\int_0^\infty d\tau\; e^{i(\tau-t)(E_n-E_m)} \sum_l \left[\langle m|A_l^*|n\rangle f_l(t-\tau) + f_l^*(t-\tau)\langle m|A_l|n\rangle\right]; \tag{5.47}$$

(5) finally, calculate $\langle A_l(t)\rangle = \overline{\langle n(t)|A_l|n(t)\rangle}$ and compare the result with the definition (8.14).

8. Sum rule:

$$\int_{-\infty}^{+\infty}\frac{d\omega_R}{\pi}\,\omega_R^n\,\mathrm{Im}\,\widehat{\alpha}(\omega_R) = \frac{1}{\hbar}\left\langle\left[\frac{1}{\hbar^n}[\dots[A,H]\dots,H],B(0)\right]_-\right\rangle, \quad n = 1,\,3,\,5,\,\dots \tag{5.48}$$

Proof: calculate $\left(i\frac{\partial}{\partial t}\right)^n \int d\omega\; e^{-i\omega t}\,\mathrm{Im}\,\widehat{\alpha}_{AB}(\omega)$.

9. Fluctuation–dissipation theorem couples the generalized susceptibility with the correlation function. Directly from the Kubo formula we have

$$\int d\omega_R e^{-i\omega_R t}\,\mathrm{Im}\,\widehat{\alpha}_{AB}(\omega_R) = \frac{1}{2\hbar}\left[Q_{AB}(-t) - Q_{BA}(t)\right] = \frac{1}{2\hbar}\left(e^{i\beta\hbar\frac{\partial}{\partial t}} - 1\right)Q_{BA}(t) \tag{5.49}$$

and, therefore,

$$\mathrm{Im}\,\widehat{\alpha}_{AB}(\omega_R) = \frac{1}{2}\beta\omega_R\,\widehat{Q}_{BA}(\omega_R)\,\frac{e^{\beta\hbar\omega_R}-1}{\beta\hbar\omega_R}\,. \tag{5.50}$$

...?...

$$\left\langle x^2\right\rangle = \frac{\hbar}{\pi}\int_0^{+\infty} d\omega\;\alpha_I(\omega)\,\mathrm{cth}\left(\frac{\hbar\omega}{2T}\right) \approx \left\{\begin{array}{l}\text{if}\quad T \gg \hbar\omega\\ \text{for all}\quad \omega\\ \text{when}\quad \alpha_I \neq 0\end{array}\right\} = T\alpha(\omega)|_{\omega=0}\,, \tag{5.51}$$

or

$$\left(x^2\right)_\omega = 2\hbar\alpha_I(\omega)\left\{\frac{1}{2} + \frac{1}{e^{\hbar\omega/T}-1}\right\}. \tag{5.52}$$

10. Energy dissipation: if

$$f(t) = \mathrm{Re}\; f_0e^{-i\omega t} = \frac{1}{2}\left(f_0e^{-i\omega t} + \text{c.c.}\right), \tag{5.53}$$

then the heat pumped into the system per one time unit, is equal to

$$\dot{Q} = \frac{dE}{dt} = \left\langle\frac{\partial H}{\partial t}\right\rangle = \left\langle\frac{\partial H_{\rm int}}{\partial t}\right\rangle = -\langle x(t)\rangle\,\frac{\partial f}{\partial t} = -\frac{1}{4}i\omega\;\left[\widehat{\alpha}(\omega) - \widehat{\alpha}(-\omega)\right]\;|f_0|^2 \tag{5.54}$$

and, because $f(t)$ is real and $\alpha(t)$ is real too, with (2.46) we obtain finally

$$\dot{Q} = \frac{1}{2}\,\omega\;\mathrm{Im}\;\widehat{\alpha}(\omega)\;|f_0|^2 > 0\,. \tag{5.55}$$

If the system is in equilibrium, i.e. it is dynamically stable, we have $\dot{Q} > 0$, so that

$$\omega_R\,\mathrm{Im}\,\widehat{\alpha}(\omega_R) > 0 \quad\text{for all}\quad \omega_R \neq 0 \tag{5.56}$$

(see also Landau V p.413).

In a general case, if $f(t)$ operates during a finite time, i.e. if $f(t) \to 0$ for $t \to \pm\infty$, the total energy absorbed by the system is equal to

$$Q \equiv \int_{-\infty}^{+\infty} dt\, \dot{Q} = -\int_{-\infty}^{+\infty} \frac{d\omega_R}{2\pi}\, i\omega_R\, \widehat{\alpha}(\omega_R)\, |\widehat{f}(\omega_R)|^2 = \int_0^{\infty} \frac{d\omega_R}{2\pi}\, 2\omega_R\, |\widehat{f}(\omega_R)|^2\, \mathrm{Im}\, \widehat{\alpha}(\omega_R)\,. \quad (5.57)$$

For the perturbation (5.35) this expression takes the form

$$Q = \int_0^{\infty} \frac{d\omega_R}{2\pi}\, \widehat{\mathbf{f}}^*(\omega_R) \left[\frac{\omega_R}{2i} \left(\widehat{\alpha}(\omega_R) - \widehat{\alpha}(-\omega_R) \right) \right] \widehat{\mathbf{f}}(\omega_R)\,, \quad (5.58)$$

and Eq. (5.56) is to be rewritten as

$$\omega_R\, \mathrm{Im}\, \widehat{\alpha}_{kk}(\omega_R) > 0 \quad \text{for all} \quad \omega_R \neq 0\,. \quad (5.59)$$

5.4 Hydrodynamic Approximation

...

5.5 Examples

5.5.1 Longitudinal permeability

Let us consider an electron gas, and let the external "force" be an external (infinitesimal) charge with the density $\rho_{\text{ext}} \propto e^{-ikx+i\omega t} e^{\delta t}$. In this case the interaction is given by the integral

$$H_{\text{int}} = e^2 \iint dr\, dr'\, \frac{\rho(r)\, \rho_{\text{ext}}(r')}{|r - r'|}\,. \quad (5.60)$$

(Note: this is a potential interaction – all magnetic or electromagnetic effects are neglected!) Thus, here "x" corresponds to ρ, "f" is given by $\rho_{\text{ext}}/|r - r'|$, and we may introduce α as in the standard theory.

To be in accordance with Maxwell equations, the permeability is defined as $D = \epsilon E$, or $\varphi_{\text{tot}} = \varphi_{\text{ext}}/\epsilon$. Then from Maxwell equations it follows that $\epsilon = ...1/\alpha$, so that the properties of ϵ_l are the following:

...

5.5.2 Transverse permeability

Let the external "force" be a plane electromagnetic wave,

$$\mathbf{A}(xt) = \mathbf{A}_0 e^{iqx - i\omega t} + \text{h.c.}, \quad (5.61)$$

where $q^2 = \omega^2/c^2$, and we chose the Lorentz calibration $\varphi = 0$, $\nabla \cdot A = 0$. Then the interaction Hamiltonian is given by the expression

$$H_{\text{int}} = -\frac{1}{c} j(xt)\, A(xt)\,, \quad j(t) \equiv \sum_a \frac{e_a}{m_a c} p_a\,. \quad (5.62)$$

Then ...

Chapter 6

Green Functions

6.1 Introductional Remarks

...

6.2 General Theory

For two observable $A(t)$ and $B(t)$ (in the Heisenberg representation) the two-time *causal* Green function is defined by

$$\begin{aligned} G^c(t,t') \equiv \langle\!\langle A(t)|B(t')\rangle\!\rangle_c &= \frac{1}{i}\langle T_{\text{ch}} A(t)B(t')\rangle \\ &= -i\theta(t-t')\langle A(t)B(t')\rangle - i\eta\theta(t'-t)\langle B(t')A(t)\rangle \,, \end{aligned} \tag{6.1}$$

where the average $\langle\ldots\rangle$ has been defined above, see Eq. (8.14).

The retarded and advanced Green functions are useful in the $T \neq 0$ case. The *retarded* Green function is defined by

$$\begin{aligned} G^r(t,t') \equiv \langle\!\langle A(t)|B(t')\rangle\!\rangle_r &= -i\theta(t-t')\langle \left[A(t),B(t')\right]_\eta\rangle \\ &= -i\theta(t-t')\left(\langle A(t)B(t')\rangle - \eta\langle B(t')A(t)\rangle\right), \end{aligned} \tag{6.2}$$

and the *advanced* Green function, by

$$\begin{aligned} G^a(t,t') \equiv \langle\!\langle A(t)|B(t')\rangle\!\rangle_a &= +i\theta(t'-t)\langle \left[A(t),B(t')\right]_\eta\rangle \\ &= +i\theta(t'-t)\left(\langle A(t)B(t')\rangle - \eta\langle B(t')A(t)\rangle\right). \end{aligned} \tag{6.3}$$

All three functions satisfy the same differential equation

$$i\hbar\frac{dG(t,t')}{dt} = \hbar\theta(t-t')\langle\left[A(t),B(t')\right]_\eta\rangle + \langle\!\langle \{A(t)\mathcal{H}(t) - \mathcal{H}(t)A(t)\}\,|B(t')\rangle\!\rangle \tag{6.4}$$

with, however, different spectral theorems which play the role of boundary conditions. The operator $\mathcal{H}(t)$ was defined above by Eq. (8.14); for the $T=0$ case we have to use $H(t)$. However, when the Hamiltonian directly depends on time, the Green function technique becomes not too suitable, although the corresponding perturbation theory has been developed by L.V.Keldysh; it is described in [] (Landau X). Note that for Bose particles with zero rest mass such as photons and phonons, Eq. (6.4) reduces to the identity; in this case the second-order motion equation should be derived.

Below we will consider *conservative systems* only, when the Hamiltonian does not depend explicitly on time. When a conservative system is in the equilibrium state, then $G(t', t'') = G(t' - t'') = G(t)$, and we may make the Fourier transform over time,

$$G(\omega) = \int_{-\infty}^{+\infty} dt \, G(t) \, e^{i\omega t} e^{-\delta |t|}, \quad G(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \, G(\omega) \, e^{-i\omega t}. \tag{6.5}$$

The motion equation for the Green functions takes the following form,

$$\hbar\omega \langle\langle A|B\rangle\rangle_\omega = \hbar \langle [A, B]_\eta \rangle + \langle\langle AH - HA|B\rangle\rangle_\omega. \tag{6.6}$$

Directly from the definition (6.1) of the causal Green function it follows that

$$G^c(t = +\delta) - G^c(t = -\delta) = -i \langle [A, B]_\eta \rangle \,. \tag{6.7}$$

The main application of the Green function technique is:

$$\langle BA \rangle = \frac{1}{i} G^c(t = -\delta) = \frac{1}{2\pi i} \oint_O d\omega \, G^c(\omega) \,, \tag{6.8}$$

where the anticlockwise closed contour O consists of the real ω-axis and the upper half-circle.

Spectral properties of these Green functions are the following:

$$\operatorname{Re} G^r(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\omega' \, \frac{\operatorname{Im} G^r(\omega')}{\omega - \omega'} \,, \tag{6.9}$$

$G^r(\omega)$ is analytical function in the upper ω–half-plane, $\operatorname{Im}\omega > 0$,

$$\operatorname{Re} G^a(\omega) = +\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\omega' \, \frac{\operatorname{Im} G^a(\omega')}{\omega - \omega'} \,, \tag{6.10}$$

$G^a(\omega)$ is analytical function in the lower ω–half-plane, $\operatorname{Im}\omega < 0$,

$$\operatorname{Re} G^c(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\omega' \, \frac{e^{\beta\omega'} - \eta}{e^{\beta\omega'} + \eta} \, \frac{\operatorname{Im} G^c(\omega')}{\omega - \omega'} \,, \tag{6.11}$$

$G^c(\omega)$ is nonanalytical function on the ω–plane.

At $T = 0$ the causal Green function may be represented in the form:

$$G^c(\omega) = \int_{-\infty}^{+\infty} d\omega' \left[\frac{\rho_+(\omega')}{\omega - \omega' + i\delta - \mu} - \eta \frac{\rho_-(\omega')}{\omega + \omega' - i\delta - \mu} \right], \tag{6.12}$$

where

$$\rho_\pm(\omega) = \sum_m \rho_\pm^{(m)} \, \delta\left(\omega - \varepsilon_\pm(m)\right), \tag{6.13}$$

$$\begin{aligned} \hbar\varepsilon_+^{(m)} &= E_m^{\text{exact}} - E_0^{\text{exact}}, \\ \hbar\varepsilon_-^{(m)} &= E_0^{\text{exact}} - E_m^{\text{exact}}, \end{aligned} \tag{6.14}$$

and

$$\begin{aligned} \rho_+^{(m)} &= \langle \Psi_0|A|\Psi_m\rangle \langle \Psi_m|B|\Psi_0\rangle \,, \\ \rho_-^{(m)} &= \langle \Psi_0|B|\Psi_m\rangle \langle \Psi_m|A|\Psi_0\rangle \,. \end{aligned} \tag{6.15}$$

Proof: for $t > t'$ we have

$$\begin{aligned}\langle A(t)B(t')\rangle &= e^{-iE_0^{\text{exact}}(t'-t)}\langle\Psi_0|Ae^{-iHt}e^{iHt'}B|\Psi_0\rangle \\ &= \sum_m \rho_+^{(m)} \exp\left[i\left(E_m^{\text{exact}} - E_0^{\text{exact}}\right)(t'-t)\right],\end{aligned} \tag{6.16}$$

while for $t < t'$ we can write

$$\begin{aligned}\langle B(t')A(t)\rangle &= e^{+iE_0^{\text{exact}}(t'-t)}\langle\Psi_0|Be^{-iHt'}e^{iHt}A|\Psi_0\rangle \\ &= \sum_m \rho_-^{(m)} \exp\left[-i\left(E_m^{\text{exact}} - E_0^{\text{exact}}\right)(t'-t)\right].\end{aligned} \tag{6.17}$$

Properties of the causal Green function:

1.

$$\int_{-\infty}^{+\infty} d\omega\ \left[\rho_+(\omega) + \rho_-(\omega)\right] = \langle\Psi_0|AB + BA|\Psi_0\rangle\,. \tag{6.18}$$

2.

$$\begin{cases} \rho_+(\omega) = 0 & \text{for}\quad \omega < \epsilon_+ \equiv \min_m \varepsilon_+^{(m)}\,, \\ \rho_-(\omega) = 0 & \text{for}\quad \omega > \epsilon_- \equiv \max_m \varepsilon_-^{(m)}\,, \end{cases} \tag{6.19}$$

where $\epsilon_- \le \mu \le \epsilon_+$.

3. $G(\omega) \propto 1/\omega$ at $\omega \to \infty$.

4. If $A = B^*$, then $\rho_\pm(\omega) \ge 0$.

In a general case the *spectral function* is defined as

$$J(\omega) = -\frac{1}{2\pi i}\left(e^{\beta\omega} - \eta\right)^{-1}\left[G^r(\omega + i\delta) - G^a(\omega - i\delta)\right]. \tag{6.20}$$

Using the complete basis of eigenvectors of the operator $\mathcal{H}$, $\mathcal{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$, the spectral function may be written as

$$J(\omega) = Q^{-1}\sum_{mn}\langle\Psi_n|A|\Psi_m\rangle\langle\Psi_m|B|\Psi_n\rangle e^{-\beta E_m}\,\delta\left(\frac{E_m - E_n}{\hbar} - \omega\right). \tag{6.21}$$

The Green functions may be expressed through the spectral function:

$$G^{r,a}(\omega) = \int_{-\infty}^{+\infty} d\omega'\,\frac{e^{\beta\omega'} - \eta}{\omega - \omega' \pm i\delta}\,J(\omega')\,, \tag{6.22}$$

$$G_c(\omega) = \mathcal{P}\int_{-\infty}^{+\infty} d\omega'\,\frac{e^{\beta\omega'} - \eta}{\omega - \omega'}\,J(\omega') - i\pi\left(e^{\beta\omega} + \eta\right)J(\omega)\,. \tag{6.23}$$

6.3 Fermi Particles

6.3.1 Definitions

Recall: $\widehat{c}\widehat{c}^* + \widehat{c}^*\widehat{c} = 1$ ($\widehat{c}$ and $\widehat{c}^*$ are the annihilation and creation operators respectively; hat will be omitted in what follows); in the Heisenberg representation $c(t) \propto$ ...

Let: $\varepsilon_F = 0$ (the origin of energy may be chosen arbitrary).

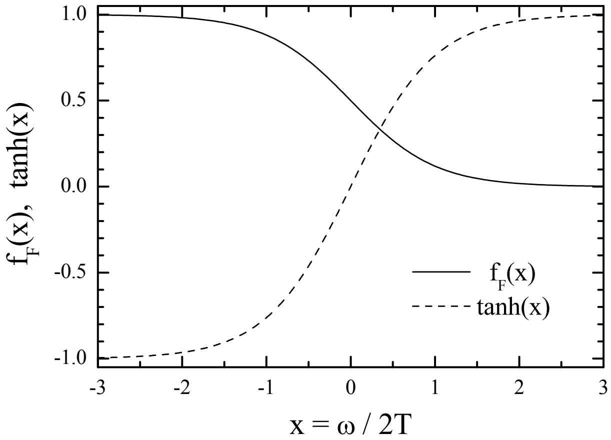


Figure 6.1: The functions $f_F(x)$ (solid curve) and $\tanh(x)$ (dash curve).

Define the dimensionless variable $x = \omega/2T$ ($k_B = 1$), and introduce the Fermi-Dirac distribution function

$$f_F(\omega) = \frac{1}{e^{\omega/T} + 1} = \frac{1}{2}\left[1 - \tanh(x)\right], \tag{6.24}$$

so that $\tanh(x) = 1 - 2f_F(\omega)$. The function (6.24) is shown in Fig. 6.1.

The function $f_F(\omega)$ has simple poles at $\omega = z_n = i(2n+1)\pi T$; the residues at these poles are equal to $-T$.

The *causal* Green function is defined as

$$G^c(t) = \frac{1}{i}\langle T_{\text{ch}} c(t)c^*(0)\rangle = \frac{1}{i}\Theta(t)\langle c(t)c^*(0)\rangle - \frac{1}{i}\Theta(-t)\langle c^*(0)c(t)\rangle\,. \tag{6.25}$$

Its Fourier transform in the simplest case is

$$G^c(\omega) = \frac{1 - f_F(\omega)}{\omega - \varepsilon_m + i\delta} + \frac{f_F(\omega)}{\omega - \varepsilon_m - i\delta}\,. \tag{6.26}$$

The *retarded* Green function $G^{(+)} = G^r$ is defined as

$$G^r(t) = \frac{1}{i}\Theta(t)\langle c(t)c^*(0) + c(0)c^*(t)\rangle\,. \tag{6.27}$$

Its Fourier transform is

$$G^r(\omega) = \frac{1}{\omega - \varepsilon_m + i\delta}\,. \tag{6.28}$$

The function $G^r(\omega)$ is analytical in the upper half-plane of the complex ω plane.

The *advanced* Green function $G^{(-)} = G^a$ is defined by the expression

$$G^a(t) = -\frac{1}{i}\Theta(-t)\langle c(t)c^*(0) + c(0)c^*(t)\rangle\,, \tag{6.29}$$

$$G^a(\omega) = \frac{1}{\omega - \varepsilon_m - i\delta}\,. \tag{6.30}$$

The function $G^a(\omega)$ is analytical on the lower half-plane of the complex ω plane.

All three Green functions introduced above, are dynamical (time-dependent) functions. *The perturbation theory technique exists only for the causal Green function and only in the $T = 0$ case.*

Relationships between different Green functions:
First, all dynamical functions depend on time as $G(t) \propto e^{-i\varepsilon_m t}$.
The real parts of all three functions are equal each other:

$$\mathrm{Re}\, G^c(\omega) = \mathrm{Re}\, G^a(\omega) = \mathrm{Re}\, G^r(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{+\infty} d\omega_1\, \frac{J(\omega_1)}{\omega - \omega_1}\,, \tag{6.31}$$

where $J(\omega)$ is the *spectral function.*

Imaginary parts of the Green functions may be expressed through the spectral function $J(\omega)$:

$$\mathrm{Im}\, G^a(\omega) = J(\omega)\,, \tag{6.32}$$

$$\mathrm{Im}\, G^r(\omega) = -J(\omega)\,, \tag{6.33}$$

$$\mathrm{Im}\, G^c(\omega) = -\tanh(\omega/2T)\; J(\omega)\,. \tag{6.34}$$

Combining (6.31) and (6.33), the Green functions may be expressed through the function $J(\omega)$. For example,

$$G^r(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{+\infty} d\omega_1\, \frac{J(\omega_1)}{\omega_1 - \omega - i\delta}\,. \tag{6.35}$$

For the system of noninteracting particles, the advanced and retarded Green functions, as well as the real part of the causal Green function, do not depend on temperature. The temperature dependence of the imaginary part of the causal function is described by the equation

$$\mathrm{Im}\, G^c(\omega; T \neq 0) = \tanh\left(-\frac{\omega - \epsilon_F}{2k_B T}\right) \mathrm{Im}\, G^a(\omega; T = 0)\,, \tag{6.36}$$

where ω is assumed to be real.

The main application of the Green function technique is that an average value of any operator can be calculated through the integral of the Green function, because

$$\langle c^* c\rangle = \frac{1}{i} G^c(t = -\delta) = \frac{1}{2\pi i}\oint_O d\omega\; G^c(\omega) = \frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} d\omega\; f_F(\omega) J(\omega)\,, \tag{6.37}$$

where the closed contour O consists of the real axis plus the upper half-cycle. In the last equality we used the Kramers–Kronig relation.

Finally, let us introduce the *Matsubara* Green function. It does not depend on time and, thus, describes the statistical (equilibrium) properties of the system only. However, it allows to develop the perturbation theory technique for the $T \neq 0$ case.

Recall that $\beta = 1/T$ ($k_B = 1$), and introduce the variable τ defined within the interval

$$-\beta < \tau < +\beta\,. \tag{6.38}$$

Define the Matsubara representation for an operator A as

$$A(\tau) = e^{\tau H_0} A\, e^{-\tau H_0} \tag{6.39}$$

(indicate a formal analogy with the Heisenberg representation if we put $\tau = it$).

The Matsubara Green function is defined as

$$G^m(\tau) = -\langle T_m c(\tau)\bar{c}(0)\rangle = -\Theta(\tau)\langle c(\tau)\bar{c}(0)\rangle + \Theta(-\tau)\langle \bar{c}(0)c(\tau)\rangle\,, \tag{6.40}$$

where T_m is ... Directly from the definition we have

$$G^m(-\tau) = -G^m(-\tau+\beta)\,, \tag{6.41}$$

so that $G^m(\tau)$ is a periodic function of τ with the period 2β and, therefore, in the interval $(-\beta,+\beta)$ the function $G^m(\tau)$ may be expanded into the Fourier series over the "harmonics"

$$\omega_n = (2n+1)\pi T, \quad \text{where} \quad T = \frac{2\pi}{2\beta} \quad \text{and} \quad n = 0, \pm 1, \pm 2, \dots \tag{6.42}$$

The Fourier series is

$$G^m(\tau) = \frac{1}{\beta}\sum_{n=-\infty}^{+\infty} G^m(\omega_n)\, e^{-i\omega_n\tau}, \tag{6.43}$$

and the Fourier transform of $G^m(\tau)$ is

$$G^m(\omega_n) = \int_{-\beta}^{+\beta} \dots = \int_0^{+\beta} d\tau\; e^{i\omega_n\tau} G^m(\tau)\,, \tag{6.44}$$

so that

$$G^m(-\omega_n) = [G^m(+\omega_n)]^* \tag{6.45}$$

and

$$G^m(\omega_n > 0) = G^r(i\omega_n)\,. \tag{6.46}$$

In the simplest case we obtain

$$G^m(\tau > 0) = -e^{-\tau\varepsilon_n}\left(1 - f_F(\varepsilon_n)\right)\,, \tag{6.47}$$

$$G^m(\omega_n) = +\frac{1}{i\omega_n - \varepsilon_n}\,. \tag{6.48}$$

6.3.2 A general case

For two observable $A(t)$ and $B(t)$ the Green functions are defined by

$$G^c(t,t') = \frac{1}{i}\langle T_{\text{ch}} A(t)B(t')\rangle = -i\theta(t-t')\langle A(t)B(t')\rangle + i\theta(t'-t)\langle B(t')A(t)\rangle\,, \tag{6.49}$$

$$G^r(t,t') = -i\theta(t-t')\langle [A(t),B(t')]_-\rangle = -i\theta(t-t')\left(\underbrace{\langle A(t)B(t')\rangle}_{\text{particle}} + \langle B(t')A(t)\rangle\right)\,, \tag{6.50}$$

$$G^a(t,t') = +i\theta(t'-t)\langle [A(t),B(t')]_-\rangle = +i\theta(t'-t)\left(\langle A(t)B(t')\rangle + \underbrace{\langle B(t')A(t)\rangle}_{\text{hole}}\right)\,. \tag{6.51}$$

Different Green functions are coupled by the relationship

$$G^{r,a}(\omega) = \operatorname{Re} G^c(\omega) \pm i\coth\left(\frac{\omega}{2T}\right)\operatorname{Im} G^c(\omega)\,, \tag{6.52}$$

where $\coth(x) = \cosh(x)/\sinh(x)$.

The real and imaginary parts of the causal Green function are coupled by the relation

$$\operatorname{Re} G^c(\omega) = -\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} d\omega'\, \frac{\coth(\beta\omega')}{\omega-\omega'}\, \operatorname{Im} G^c(\omega')\,. \tag{6.53}$$

At $T = 0$ this relation takes the form

$$\operatorname{Re} G^c(\omega) = \frac{1}{\pi}\,\mathcal{P}\left\{\int_{-\infty}^{\mu} - \int_{\mu}^{+\infty}\right\} d\omega'\, \frac{\operatorname{Im} G^c(\omega')}{\omega-\omega'}\ . \tag{6.54}$$

For a normal (non superconductive) Fermi system, where the standard perturbation theory technique may be used and the Dyson equation is valid, one has

$$G(k,\omega) = [\omega - \omega_k - \Sigma(k,\omega)]^{-1}\,, \tag{6.55}$$

and the $T = 0$ retarded Green function has pole(s) in the lower ω–half-plane at $\omega = \omega_0' - i\Gamma_0'$ which describes a quasiparticle with the energy ω_0' and the lifetime $1/\Gamma_0'$, while the $T = 0$ advanced Green function has a pole in the upper ω–half-plane at $\omega = \omega_0' + i\Gamma_0'$ which describes a quasi-hole. Near the pole the Green function takes the form

$$G^{r,a}(\omega) \approx \frac{1 - \partial\Sigma(k_0,\omega_0)/\partial\omega}{\omega - \omega_0' \pm i\Gamma_0'}\ , \tag{6.56}$$

so that

$$G^c(k,t) \approx \frac{1}{i} Z_{k_0} e^{-i\omega_0' t}\left[\theta(t)e^{-\Gamma_0' t} - \theta(-t)e^{\Gamma_0' t}\right], \tag{6.57}$$

where $Z_{k_0} = 1 - \partial\Sigma(k_0,\omega_0)/\partial\omega$ and $0 < Z_{k_0} < 1$.

Note that the one-particle Green function $\langle\!\langle c_m | c_n^* \rangle\!\rangle$ may have poles corresponding to one-particle excitations only.

6.3.3 Electron system

Coordinate basis

Let us consider the Hamiltonian in the coordinate representation,

$$H = \sum_{l=1}^{N} H_0(\mathbf{r}_l) + \frac{1}{2}\sum_{l\neq l'} v(\mathbf{r}_l - \mathbf{r}_{l'})\,, \quad H_0(\mathbf{r}) = -\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m} + U(\mathbf{r})\,, \tag{6.58}$$

and introduce the field operator

$$\Psi(\xi) = \sum_l \varphi_l(\xi)\,\widehat{c}_l\,, \quad \Psi(\xi)\Psi^*(\xi') - \Psi^*(\xi')\Psi(\xi) = \delta(\xi-\xi')\,, \tag{6.59}$$

where $\varphi_l(\xi)$ is the wavefunction of the state $|l\rangle$, and $\xi \equiv (\mathbf{r},\sigma,t)$. Introduce the causal Green function as

$$G^c(\xi,\xi') = \frac{1}{i}\langle T_{\rm ch}\Psi(\xi)\Psi^*(\xi')\rangle\,. \tag{6.60}$$

Then the average value of a one-particle operator $F = \sum_l f(\xi_l)$ is equal to

$$\overline{F} = i \lim_{t'\to t+0}\lim_{\mathbf{r}'\to\mathbf{r}} \int d\mathbf{r}\; f(\xi)\, G^c(\xi,\xi')\,. \tag{6.61}$$

The Green function (6.60) satisfies the motion equation

$$\left[i\hbar\frac{\partial}{\partial t_1} - H_0(\mathbf{r}_1)\right] G^c(\xi_1,\xi_1') = \hbar\,\delta(\xi_1-\xi_1') - \int d\mathbf{r}_2\; v(\mathbf{r}_1-\mathbf{r}_2)\, G^c(1,2,2^+,1')\Big|_{t_2=t_1}, \tag{6.62}$$

where $t_2^+ = t_2+\delta$ and

$$G^c(1,2,3,4) = \frac{1}{i}\langle T_{\text{ch}}\Psi(\xi_1)\Psi(\xi_2)\Psi^*(\xi_3)\Psi^*(\xi_4)\rangle\,. \tag{6.63}$$

If G_0 is the Green function for noninteracting particles, $v\equiv 0$, then the functions G and G_0 are coupled by the Dyson equation,

$$G(x,x';\omega) = G_0(x,x';\omega) + \int dx''\,dx'''\; G_0(x,x'';\omega)\,\Sigma(x'',x''';\omega)\,G(x''',x';\omega)\,. \tag{6.64}$$

Nonorthogonal basis

Let $\{\varphi_m\}$ is a complete but nonorthogonal basis,

$$\langle\varphi_m|\varphi_n\rangle = S_{mn}\;. \tag{6.65}$$

The creation-annihilation operators for this basis satisfy the commutation relation

$$[c_{m\sigma}, c^*_{n\sigma'}]_+ = \delta_{\sigma\sigma'}\left(\mathbf{S}^{-1}\right)_{nm}, \tag{6.66}$$

where $\mathbf{S}\equiv\{S_{mn}\}$, and σ, σ' stand for spins. The Hamiltonian in the nonortogonal basis takes the form

$$H = \sum_{mn}\langle\varphi_m|H_0|\varphi_n\rangle\, c^*_m c_n + \frac{1}{2}\sum_{ijkl}\langle\varphi_i\varphi_j|v|\varphi_k\varphi_l\rangle\, c^*_i c^*_j c_l c_k\,. \tag{6.67}$$

Introduce the causal Green function

$$G^c_{mn}(t) = \frac{1}{i}\langle T_{\text{ch}} c_m(t) c^*_n(0)\rangle\,. \tag{6.68}$$

Then at $T=0$ we have

$$\langle c^*_n c_m\rangle = \frac{1}{i}G^c_{mn}(t=-\delta) = \frac{1}{2\pi i}\oint_O d\omega\; G^c_{mn}(\omega)\,, \tag{6.69}$$

$$G^c_{mn}(t=+\delta) - G^c_{mn}(t=-\delta) = -i\langle[c_m,c^*_n]_+\rangle\,. \tag{6.70}$$

The energy of the ground state of the system is

$$\begin{aligned} E_0^{\text{exact}} &= \frac{1}{2}\lim_{t\to-\delta}\sum_{mn}\left[\frac{1}{i}H_{mn}G^c_{nm}(t) + \hbar S_{mn}\frac{dG^c_{nm}(t)}{dt}\right] \\ &= \frac{1}{4\pi i}\sum_{mn}\oint_O d\omega\;\left(H_{mn}+\hbar\omega S_{mn}\right)G^c_{nm}(\omega)\,. \end{aligned} \tag{6.71}$$

The Green function (6.68) satisfies the motion equation

$$\sum_l\left(\hbar\omega S_{kl} - H_{kl}\right)G^c_{ln}(\omega) = \hbar\delta_{kn} + \sum_{jlm} v_{kjlm}\,\langle\langle c^*_j c_m c_l|c^*_n\rangle\rangle^c_\omega\,, \tag{6.72}$$

and the Dyson equation takes the form

$$G^c_{mn}(\omega) = G^{c0}_{mn}(\omega) + \sum_{kl}G^{c0}_{mk}(\omega)\,\Sigma_{kl}(\omega)\,G^c_{ln}(\omega)\,. \tag{6.73}$$

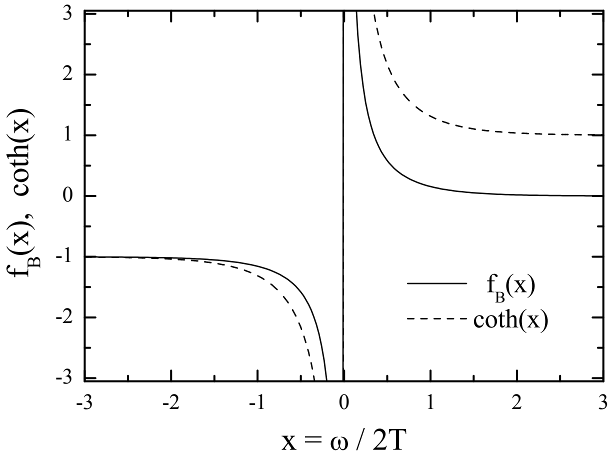


Figure 6.2: The function $f_B(x)$ (solid curve) and $\coth(x)$ (dash curve)

6.4 Bose Particles

Recall: $aa^* - a^*a = 1$, where in the Heisenberg representation $a(t) \propto e^{-i\omega_0 t}a$. Let $\omega > 0$, and define $x = \omega/2T$.

Introduce the Bose-Einstein distribution function

$$f_B(\omega) = \frac{1}{e^{\omega/T} - 1} = \frac{1}{2}\left[-1 + \coth(x)\right] \approx \begin{cases} T/\omega & \text{if} \quad \omega \ll T, \\ \exp(-\omega/T) & \text{if} \quad \omega \gg T, \end{cases} \tag{6.74}$$

so that $\coth(x) = 1 + 2f_B(\omega)$ (see Fig. 6.2). The function $f_B(\omega)$ has simple poles at $\omega = z_n = i(2n)\pi T$, residues in which are equal to $+T$.

Few useful formulas:

$$f_B(-\omega) = -1 - f_B(+\omega)\,, \tag{6.75}$$

$$f'_B(\omega) \equiv \frac{df_B(\omega)}{d\omega} = -\frac{1}{T} f_B(\omega)\left[1 + f_B(\omega)\right] = \frac{1}{4T}[1 - \text{cotanh}(x)][1 + \text{cotanh}(x)]\,. \tag{6.76}$$

For Bose particles $\operatorname{Im} G^c(\omega) < 0$.

Different Green functions are coupled by the relationship

$$G^{r,a}(\omega) = \operatorname{Re} G^c(\omega) \pm i \tanh\left(\frac{\omega}{2T}\right) \operatorname{Im} G^c(\omega)\,. \tag{6.77}$$

The real and imaginary parts of the causal Green function are coupled by the relation

$$\operatorname{Re} G^c(\omega) = -\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} d\omega'\, \frac{\tanh(\beta\omega')}{\omega - \omega'} \operatorname{Im} G^c(\omega')\,. \tag{6.78}$$

Chapter 7

Phonons

Phonons (as well as photons) are Bose-particles with *zero* rest mass, so that their number in the system is not conserved (the corresponding chemical potential is zero). That leads to some difference in the Green function technique for their description. In particular, the motion equation should be of the second order. Besides, phonons are important for applications of solid state physics. For these reasons we describe the Green function technique for phonons in this Chapter.

7.1 Hamiltonian

Let us consider an infinite (linear, one-dimensional) atomic chain. Define: let u_n be the displacement operator of the n-th atom from its equilibrium position $l_n = na$, so that the coordinate of the atom is $x_n = l_n + u_n$, and let p_n be the corresponding momentum. The coordinate and momentum satisfy the standard quantum-mechanical relations,

$$u_n p_n - p_n u_n = i\hbar \,, \quad \text{others} = 0 \,. \tag{7.1}$$

Expand the potential energy U of the system in Taylor series over the displacements u_n:

$$U(\ldots,\, x_{-1},\, x_0,\, x_1, \ldots) = \frac{1}{2!} \sum_{n_1,\, n_2} \frac{\partial^2 U}{\partial u_{n_1} \partial u_{n_2}} \, u_{n_1} u_{n_2} + \ldots \,, \tag{7.2}$$

where the zero-order term is constant and, therefore, can be omitted, and the first-order terms are zero, because the expansion is done over the equilibrium state. Thus, the Hamiltonian in the harmonic approximation is the following,

$$H = \sum_{n=-\infty}^{+\infty} \frac{p_n^2}{2m_n} + \frac{1}{2} \sum_{n_1, n_2} \alpha(n_1, n_2) \, u_{n_1} u_{n_2} \,, \tag{7.3}$$

where

$$\alpha(n_1, n_2) = \frac{\partial^2 U}{\partial u_{n_1} \partial u_{n_2}} \,. \tag{7.4}$$

The motion equation has the following form,

$$m_n \ddot{u}_n = -\frac{\partial U}{\partial u_n} = -\sum_{n_1} \alpha(n, n_1) u_{n_1} \,. \tag{7.5}$$

Thus, we come to the standard problem – to look for eigenvectors $u_k = \sum_n \varphi_{kn} u_n$ and eigenfrequencies ω_k so that $\ddot{u}_k + \omega^2 u_k = 0$.

For a pairwise potential, the potential energy takes the following form,

$$U(\ldots) = \frac{1}{2} \sum_{n_1 \neq n_2} V(x_{n_1} - x_{n_2}) \,, \tag{7.6}$$

and the dynamical matrix $\alpha(n_1, n_2)$ is determined by the expressions

$$\alpha(n_1, n_2) = \frac{\partial^2 V(x_{n_1} - x_{n_2})}{\partial u_{n_1} \partial u_{n_2}} \quad \text{if} \quad n_1 \neq n_2 \tag{7.7}$$

and

$$\alpha(n, n) = \sum_{n_1 (n_1 \neq n)} \frac{\partial^2 V(x_n - x_{n_1})}{\partial u_n^2} \,. \tag{7.8}$$

Define:
A is the matrix with the elements $\alpha(n_1, n_2)$, and
D is the matrix with the elements $\alpha(n_1, n_2)/\sqrt{m_{n_1} m_{n_2}}$.

7.2 Green Function Approach

7.2.1 Causal Green function (T = 0)

The *causal* Green function is defined as (e.g., see Kosevich)

$$\mathcal{G}^c(t; n_1, n_2) = \sqrt{m_{n_1} m_{n_2}} \, \frac{1}{i\hbar} \, \langle T_{\text{ch}} \, u_{n_1}(t) \, u_{n_2}(0) \rangle \,, \tag{7.9}$$

where $u(t)$ is the displacement operator in the Heisenberg representation,

$$u_n(t) = e^{i(H/\hbar)t} u_n e^{-i(H/\hbar)t}. \tag{7.10}$$

Using the commutation relations (7.1), it is easy to check that the coordinates $u(t)$ satisfy the motion equations

$$\frac{du_n(t)}{dt} = \frac{i}{\hbar} \left[H u_n(t) - u_n(t) H \right] = \frac{i}{2m_n \hbar} (p_n^2 u_n - u_n p_n^2) = \frac{p_n(t)}{m_n} \,, \tag{7.11}$$

$$\frac{dp_n(t)}{dt} = \frac{i}{\hbar} \left[H p_n(t) - p_n(t) H \right] = \frac{i}{2\hbar} \sum_{n_1, n_2} \alpha(n_1, n_2) (u_{n_1} u_{n_2} p_n - p_n u_{n_1} u_{n_2}) = -\sum_{n_3} \alpha(n, n_3) u_{n_3} \,. \tag{7.12}$$

The quantum motion equations (7.11–7.12) has the same form as the classical ones. This is the result of the harmonic approximation (7.3): for the harmonic oscillator the quantum motion equation has the same form as the classical ones.

The Fourier transform of the Green function is defined as

$$\mathcal{G}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \, e^{-i\omega t} \mathcal{G}(\omega) \,, \tag{7.13}$$

$$\mathcal{G}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{+i\omega t} e^{-\delta |t|} \mathcal{G}(t) \,. \tag{7.14}$$

The real and imaginary parts of $\mathcal{G}^c(\omega)$ are coupled by the Kramers–Kronig relation

$$\begin{aligned}\mathrm{Re}\,\mathcal{G}^c(\omega) &= \frac{1}{\pi}\left\{\mathcal{P}\int_0^{+\infty} - \mathcal{P}\int_{-\infty}^{0}\right\} d\omega' \, \frac{\mathrm{Im}\,\mathcal{G}^c(\omega')}{\omega'-\omega} \\ &= \frac{1}{\pi}\mathcal{P}\int_0^{+\infty} d\omega_1 \,\mathrm{Im}\,\mathcal{G}^c(\omega_1)\frac{2\omega_1}{\omega_1^2-\omega^2} \\ &= \frac{1}{\pi}\mathcal{P}\int_0^{+\infty} d\epsilon\,\frac{\mathrm{Im}\,\mathcal{G}^c(\epsilon)}{\epsilon-\omega^2}\,, \end{aligned} \tag{7.15}$$

where $\mathcal{P}\int$ means the principal value of the integral, and we introduced also the variable $\epsilon=\omega_1^2$.

From (7.15) one can see that

$$\mathrm{Re}\,\mathcal{G}^c(\omega\to\infty) \approx \left[-\frac{1}{\pi}\mathcal{P}\int_0^{+\infty} d\epsilon\,\mathrm{Im}\,\mathcal{G}^c(\epsilon)\right]\frac{1}{\omega^2} \tag{7.16}$$

and

$$\mathrm{Re}\,\mathcal{G}^c(\omega=0) = -\left[-\frac{1}{\pi}\mathcal{P}\int_0^{+\infty} d\epsilon\,\mathrm{Im}\,\mathcal{G}^c(\epsilon)/\epsilon\right] < 0\,. \tag{7.17}$$

Note that the prefactor in the definition (7.9) is chosen so that $\mathcal{G}(t)\sim$ time and $\mathcal{G}(\omega)\sim\omega^{-2}$. The function (7.9) is the one-phonon Green function, therefore its poles describe the one-phonon spectrum, i.e. the widths of peaks describe lifetimes of excitations, and Im $\mathcal{G}^c(\omega)$ is the density of phonon states.

7.2.2 Temporal Green functions (T $\neq$ 0)

Recall that the perturbation theory technique for the interacting particles exists only for the $T=0$ case and only for the causal Green function. However, when the phonon-phonon interaction is not important, the temporal Green functions for $T\neq 0$ may be useful.

Notice: the factor $\sqrt{m_{n_1}m_{n_2}}/\hbar$ will temporarily be omitted in what follows.

The *causal* Green function for $T\neq 0$ is defined as

$$\mathcal{G}^c(t) = \frac{1}{i}\,\langle T_{\mathrm{ch}}\,u(t)\,u(0)\rangle = \frac{1}{i}\Theta(t)\langle u(t)\,u(0)\rangle + \frac{1}{i}\Theta(-t)\langle u(0)\,u(t)\rangle\,. \tag{7.18}$$

For the simplest case of one oscillator only, we can easily obtain that

$$\mathcal{G}^c(t) \propto \frac{1}{i}e^{-i\omega_0|t|} + \frac{1}{i}f_B(\omega_0)\left(e^{i\omega_0 t}+e^{-i\omega_0 t}\right), \tag{7.19}$$

and the Fourier transform of (7.19) is

$$\mathcal{G}^c(\omega) = \frac{1+f_B(|\omega|)}{\omega^2-\omega_0^2+i\delta} - \frac{f_B(|\omega|)}{\omega^2-\omega_0^2-i\delta}\,. \tag{7.20}$$

Note that

$$\mathcal{G}^c(\omega) = \mathcal{G}^c(-\omega) = \mathcal{G}^c(|\omega|) \tag{7.21}$$

and

$$\mathrm{Im}\,\mathcal{G}^c(\omega) \leq 0\,. \tag{7.22}$$

The *retarded* Green function is

$$\mathcal{G}^r(t) = \frac{1}{i}\Theta(t)\langle u(t)u(0) - u(0)u(t)\rangle\,, \tag{7.23}$$

and for a single oscillator it takes the form

$$\mathcal{G}^r(\omega) = \frac{1}{\omega^2 - \omega_0^2 + i\delta\,\mathrm{sign}(\omega)}\,. \tag{7.24}$$

Recall that $\mathcal{G}^r(\omega)$ is analytical in the upper half-plane of the complex ω plane. The function $\mathcal{G}^r(t)$ describes outgoing waves: $\mathcal{G}^r(t) = 0$ for $t < 0$, and $\mathcal{G}^r(t) = -(\sin\omega_0 t)/\omega_0$ for $t > 0$.

The *advanced* Green function is

$$\mathcal{G}^a(t) = -\frac{1}{i}\Theta(-t)\langle u(t)u(0) - u(0)u(t)\rangle\,, \tag{7.25}$$

$$\mathcal{G}^a(\omega) = \frac{1}{\omega^2 - \omega_0^2 - i\delta\,\mathrm{sign}(\omega)} = [\mathcal{G}^r(\omega)]^*\,. \tag{7.26}$$

Recall that $\mathcal{G}^a(\omega)$ is analytical in the lower half-plane. The function $\mathcal{G}^a(t)$ describes incoming waves: $\mathcal{G}^a(t) = (\sin\omega_0 t)/\omega_0$ for $t < 0$, and $\mathcal{G}^a(t) = 0$ for $t > 0$.

Relationships between different Green functions: introducing the spectral function $J(\omega)$,

$$J(\omega) = -\mathrm{Im}\,\mathcal{G}^c(\omega; T = 0) = J(-\omega)\,, \tag{7.27}$$

we have for the imaginary parts of the Green functions the following relations,

$$\mathrm{Im}\,\mathcal{G}^c(\omega) = -\left[1 + 2f_B(|\omega|)\right] J(\omega) = -\coth\left(\frac{|\omega|}{2T}\right) J(\omega)\,, \tag{7.28}$$

$$\mathrm{Im}\,\mathcal{G}^r(\omega) = -\mathrm{sign}(\omega)\, J(\omega)\,, \tag{7.29}$$

$$\mathrm{Im}\,\mathcal{G}^a(\omega) = +\mathrm{sign}(\omega)\, J(\omega)\,, \tag{7.30}$$

and for the real parts, the relations

$$\begin{aligned}\mathrm{Re}\,\mathcal{G}^c(\omega) = \mathrm{Re}\,\mathcal{G}^a(\omega) = \mathrm{Re}\,\mathcal{G}^r(\omega) &= \frac{1}{\pi}\left\{\mathcal{P}\int_0^{+\infty} - \mathcal{P}\int_{-\infty}^0\right\} d\omega_1\, \frac{J(\omega_1)}{\omega - \omega_1} \\ &= \frac{1}{\pi}\,\mathcal{P}\int_0^{+\infty} d\omega_1\, \frac{2\omega_1 J(\omega_1)}{\omega^2 - \omega_1^2}\,. \end{aligned} \tag{7.31}$$

Combining Eqs. (8.14) and (8.14), we can express the retarded Green function (8.14) through the function $J(\omega)$:

$$\mathcal{G}^r(\omega > 0) = \frac{1}{\pi}\mathcal{P}\int_0^{+\infty} d\omega_1\, \frac{2\omega_1 J(\omega_1)}{\omega^2 - \omega_1^2 + i\delta}\,. \tag{7.32}$$

Notice that Eq. (8.14) is valid for $\omega > 0$ only, while for the $T = 0$ case Eq. (8.14) is valid for all ω.

Application: an average value of squared displacement is equal to

$$\langle uu\rangle = -\frac{1}{i}\,\mathcal{G}^c(t = 0) = -\frac{1}{2\pi i}\int_O d\omega\; \mathcal{G}^c(\omega) = \frac{1}{\pi}\,\mathcal{P}\int_0^{+\infty} d\omega\;\left[1 + 2f_B(\omega)\right] J(\omega)\,. \tag{7.33}$$

7.2.3 Matsubara Green function

Recall: $\beta = 1/T$, the variable τ is defined within the interval $-\beta < \tau < +\beta$, and the Matsubara representation is defined as

$$A(\tau) = e^{\tau H_0} A e^{-\tau H_0}. \tag{7.34}$$

Then the Matsubara Green function is defined as

$$\mathcal{G}^m(\tau) = -\langle T_m u(\tau) u(0)\rangle = -\Theta(\tau)\langle u(\tau)u(0)\rangle - \Theta(-\tau)\langle u(0)u(\tau)\rangle\,. \tag{7.35}$$

From the definition (7.35) we have

$$\mathcal{G}^m(-\tau) = +\mathcal{G}^m(+\tau)\,, \tag{7.36}$$

so that $\mathcal{G}^m(\tau)$ is again periodic with the period 2β, and in the interval $(-\beta, +\beta)$ the Green function may be expanded into the Fourier series over the "harmonics"

$$\omega_n = (2n)\pi T, \quad \text{where} \quad T = \frac{2\pi}{2\beta} \quad \text{and} \quad n = 0,\, \pm 1,\, \pm 2,\, \ldots \tag{7.37}$$

The Fourier transform of the Green function is

$$\mathcal{G}^m(\tau) = \frac{1}{\beta}\sum_{n=-\infty}^{+\infty} \mathcal{G}^m(\omega_n) e^{-i\omega_n \tau}, \quad \mathcal{G}^m(\omega_n) = \int_{-\beta}^{+\beta} \ldots = \int_0^{+\beta} d\tau\; e^{i\omega_n \tau}\mathcal{G}^m(\tau)\,, \tag{7.38}$$

so that

$$\mathcal{G}^m(-\omega_n) = [\mathcal{G}^m(+\omega_n)]^* \tag{7.39}$$

and

$$\mathcal{G}^m(\omega_n > 0) = \mathcal{G}^r(i\omega_n)\,. \tag{7.40}$$

For the simplest case of one harmonic oscillator we have

$$\mathcal{G}^m(\tau > 0) = -e^{-\tau\omega_0}\left(1 + f_B(\omega_0)\right) - e^{+\tau\omega_0} f_B(\omega_0) \tag{7.41}$$

and

$$\mathcal{G}^m(\omega_n) = -\frac{1}{\omega_n^2 + \omega_0^2}\;. \tag{7.42}$$

7.3 Motion Equation for the Causal Green Function

Using the definition (8.14),

$$\mathcal{G}^c(t; n_1, n_2) = C_{n_1 n_2}\left\{\Theta(t)\langle u_{n_1}(t)\; u_{n_2}(0)\rangle + \Theta(-t)\langle u_{n_2}(0)\; u_{n_1}(t)\rangle\right\}, \tag{7.43}$$

where $C_{n_1 n_2} = \sqrt{m_{n_1} m_{n_2}}/i\hbar$, and differentiating it twice over t,

$$\frac{d\mathcal{G}^c(t; n_1, n_2)}{dt} =$$

$$= C_{n_1 n_2}\left\{\delta(t)\underbrace{\langle u_{n_1}(t)\; u_{n_2}(0)\rangle}_{=0} + \Theta(t)\left\langle \frac{du_{n_1}(t)}{dt}\; u_{n_2}(0)\right\rangle + \Theta(-t)\left\langle u_{n_2}(0)\; \frac{du_{n_1}(t)}{dt}\right\rangle\right\}$$

$$= C_{n_1n_2}\frac{1}{m_{n_1}}\left\{\Theta(t)\langle p_{n_1}(t)\, u_{n_2}(0)\rangle + \Theta(-t)\langle u_{n_2}(0)\, p_{n_1}(t)\rangle\right\}\,, \tag{7.44}$$

$$\frac{d^2\mathcal{G}^c(t;n_1,n_2)}{dt^2} =$$

$$= C_{n_1n_2}\frac{1}{m_{n_1}}\left\{\delta(t)\,\underbrace{\langle p_{n_1}\, u_{n_2} - u_{n_2}\, p_{n_1}\rangle}_{=-i\hbar\delta_{n_1n_2}} + \Theta(t)\left\langle\frac{dp_{n_1}(t)}{dt}\, u_{n_2}(0)\right\rangle + \Theta(-t)\left\langle u_{n_2}(0)\,\frac{dp_{n_1}(t)}{dt}\right\rangle\right\}$$

$$= C_{n_1n_2}\frac{1}{m_{n_1}}\left\{-i\hbar\,\delta(t)\,\delta_{n_1n_2} - \sum_{n_3}\alpha(n_1,n_3)\,\underbrace{\left[\Theta(t)\langle u_{n_3}(t)\, u_{n_2}(0)\rangle + \Theta(-t)\langle u_{n_2}(0)\, u_{n_3}(t)\rangle\right]}_{=\mathcal{G}^c(t;n_3,n_2)/C_{n_3n_2}}\right\}$$

$$= -i\hbar\,\delta(t)\,\delta_{n_1n_2}C_{n_1n_2}\frac{1}{m_{n_1}} - \sum_{n_3}\alpha(n_1,n_3)\,\frac{C_{n_1n_2}}{C_{n_3n_2}}\frac{1}{m_{n_1}}\,\mathcal{G}^c(t;n_3,n_2)\,, \tag{7.45}$$

we finally obtain the motion equation

$$\frac{d^2\mathcal{G}^c(t;n_1n_2)}{dt^2} + \sum_{n_3}\frac{\alpha(n_1,n_3)}{\sqrt{m_{n_1}m_{n_3}}}\,\mathcal{G}^c(t;n_3,n_2) = -i\,\delta(t)\,\delta_{n_1n_2}\,. \tag{7.46}$$

The Fourier transform of Eq. (7.46) takes the form

$$\left(\omega^2\mathbf{1} - \mathbf{D}\right)\mathcal{G}^{\mathbf{c}}(\omega) = \mathbf{1}, \tag{7.47}$$

where $\mathbf{D}$ is the square matrix with the elements $\alpha(n_1n_2)/\sqrt{m_{n_1}m_{n_2}}$.

Equations (8.14) and (8.14) follow from the classical Newtonian motion equations (8.14) and (8.14). If we will use Langevin motion equations instead of Newtonian ones, we obtain similar equations but with the substitution $\ddot{\mathcal{G}}^c \to \ddot{\mathcal{G}}^c - \eta\dot{\mathcal{G}}^c$ in Eq. (7.46) and $\omega^2 \to \omega(\omega - i\eta)$ in Eq. (7.47).

7.4 Spectrum

The density of vibrational modes is defined by the formula

$$g(\epsilon) = \frac{1}{N}\sum_{\mathbf{k}}\delta(\epsilon - \omega_0^2(\mathbf{k}))\,, \tag{7.48}$$

where we introduced the variable $\epsilon \equiv \omega^2$. According to the definition of the $T = 0$ causal Green function, the density of vibrations is equal to

$$g(\epsilon) = \left(-\frac{1}{N}\,\mathrm{Sp}\right)\frac{1}{\pi}\,\mathrm{Im}\,\mathcal{G}^{\mathbf{c}}(\omega)\,. \tag{7.49}$$

The spectrum (7.49) is normalized on one atom, i.e. the total number of vibrational modes with frequencies from ω^2 to $\omega^2 + d\epsilon$ is equal to $Ng(\epsilon)\,d\epsilon$.

The *frequency distribution function* is defined as $\rho(\omega) = 2N\omega g(\omega^2)$. It is determined by the relation

$$\rho(\omega) = -\frac{2}{\pi}\omega\,\mathrm{Im}\,\mathcal{G}^{\mathbf{c}}(\omega)\,, \tag{7.50}$$

i.e. the number of vibrations with frequencies from ω to $\omega + d\omega$ is equal to $\rho(\omega)\, d\omega$, and $\rho(\omega)$ is normalized by one state per atom,

$$\left(\frac{1}{N}\,\mathrm{Sp}\right) \int_0^\infty d\omega\; \rho(\omega) = 1\,. \tag{7.51}$$

Behavior of the phonon density strongly depends of the dimensionality of the system.

7.5 A General Case

Let for a complex (non Bravais) lattice, l numerate the elementary cells, $l = 1, \dots, N$; N be the total number of cells, m numerate the atoms in an elementary cell, $m = 1, \dots, r$, and $\alpha = x, y, z$. Then the atomic coordinates are described by the vector

$$\mathbf{R}_{lm} = \mathbf{l}_m + \mathbf{u}(lm)\,. \tag{7.52}$$

The Hamiltonian in a general case has the following form,

$$H = \sum_{lm\alpha} \frac{1}{2M_{lm}} p_\alpha^2(lm) + \frac{1}{2} \sum_{lm\alpha} \sum_{l'm'\alpha'} \mathcal{A}^{\alpha\alpha'}_{lm,\,l'm'}\, u_\alpha(lm)\, u_{\alpha'}(l'm')\,, \tag{7.53}$$

where

$$\mathcal{A}^{\alpha\alpha'}_{lm,\,lm} = \sum_{l'm' \neq lm} \frac{\partial^2 V(\mathbf{R}_{lm} - \mathbf{R}_{l'm'})}{\partial u_\alpha(l'm')\, \partial u_{\alpha'}(l'm')}\,, \quad \mathcal{A}^{\alpha\alpha'}_{lm,\,l'm'} = \frac{\partial^2 V(\mathbf{R}_{lm} - \mathbf{R}_{l'm'})}{\partial u_\alpha(lm)\, \partial u_{\alpha'}(l'm')}\,. \tag{7.54}$$

The motion equation is the following,

$$M_{lm}\ddot{u}_\alpha(lm) = -\sum_{l'm'\alpha'} \mathcal{A}^{\alpha\alpha'}_{lm,\,l'm'}\, u_{\alpha'}(l'm') = -M_{lm}\,\omega^2 u_\alpha(lm)\,. \tag{7.55}$$

Equation (7.55) is the equation for eigenfrequencies.

Now let us introduce the matrix $\mathbf{D} = \{D^{\alpha\alpha'}_{lm,\,l'm'}\}$,

$$D^{\alpha\alpha'}_{lm,\,l'm'} = \mathcal{A}^{\alpha\alpha'}_{lm,\,l'm'}\, (M_{lm}M_{l'm'})^{-1/2}\,. \tag{7.56}$$

The eigenfrequency equation then takes the following form,

$$(\mathbf{D} - \omega^2 \mathbf{1})\, \mathbf{B} = 0\,, \tag{7.57}$$

or

$$\sum_{l'm'\alpha'} D^{\alpha\alpha'}_{lm,\,l'm'} B^{(s)}_{\alpha'}(l'm') = \omega_s^2 B^{(s)}_\alpha(lm)\,, \tag{7.58}$$

where the quantum number $s = 1, \dots, 3Nr$ numerates the eigenvectors $B^{(s)}_\alpha(lm)$ and the eigenvalues ω_s^2. The eigenvectors should satisfy the orthonormalization condition,

$$\sum_{lm\alpha} B^{(s)}_\alpha(lm)\, B^{(s')}_\alpha(lm) = \delta_{ss'}\,, \tag{7.59}$$

and also, the completeness condition,

$$\sum_s B^{(s)}_\alpha(lm) B^{(s)}_{\alpha'}(l'm') = \delta_{ll'}\delta_{mm'}\delta_{\alpha\alpha'}\,. \tag{7.60}$$

Then, the atomic coordinates are expressed through the eigenvectors of Eq. (7.58) as follows,

$$u_\alpha(lm) = B_\alpha^{(s)}(lm)\, M_{lm}^{-1/2}. \tag{7.61}$$

One can easy check that the coordinates (7.61) satisfy the motion equation (7.55).

The phonon creation and annihilation operators a_s and a_s^* are introduced by the relations

$$u_\alpha(lm) = \sum_s (\hbar/2M_{lm}\omega_s)^{1/2}\, B_\alpha^{(s)}(lm)\,(a_s + a_s^*) \tag{7.62}$$

and

$$p_\alpha(lm) = -i\sum_s (\hbar M_{lm}\omega_s/2)^{1/2}\, B_\alpha^{(s)}(lm)\,(a_s - a_s^*)\,. \tag{7.63}$$

The Green matrix is then defined as

$$\mathbf{G} = (\omega^2\mathbf{1} - \mathbf{D})^{-1}. \tag{7.64}$$

Rewriting Eq. (7.57) as

$$(\omega^2\mathbf{1} - \mathbf{B}^{-1}\mathbf{D}\mathbf{B})\,\mathbf{B}^{-1}\mathbf{G}\mathbf{B} = \mathbf{1}, \tag{7.65}$$

we can express the matrix Green function in the following form,

$$\mathbf{G} = \mathbf{B}\mathbf{B}^{-1}(\omega^2\mathbf{1} - \mathbf{B}^{-1}\mathbf{D}\mathbf{B})^{-1}\,, \tag{7.66}$$

or

$$G_{lm,\,l'm'}^{\alpha\alpha'} = \sum_s \frac{B_\alpha^{(s)}(lm)\;[(\mathbf{B^{(s)}})^{-1}]_{\alpha'}(l'm')}{(\omega^2 - \omega_s^2)}\,. \tag{7.67}$$

7.6 Ideal Lattice

Consider the ideal periodic lattice of atoms of mass m_s. In this case $\alpha(\mathbf{n}_1, \mathbf{n}_2) = \alpha(\mathbf{n}_1 - \mathbf{n}_2)$. Stability of the system leads to the condition

$$\alpha(0) > 0\,. \tag{7.68}$$

The translation invariance of the system results in the equation

$$\sum_{\mathbf{n}} \alpha(\mathbf{n}) = 0\,. \tag{7.69}$$

In this case the spectrum always has the acoustical phonon branch, for which $\omega_0(k) \propto k$ at small k. When the elementary cell of the lattice is complex, the system has additionally optical phonons. If one considers the optical phonons *only*, Eq. (7.69) must be rewritten as

$$\sum_{\mathbf{n}} \alpha(\mathbf{n}) = m_s\omega_{\min}^2(k=0) \quad (?) \tag{7.70}$$

Making the Fourier transform over the vector index $\mathbf{n}$, the phonon states are labelled by the wave vector $\mathbf{k}$. The phonon spectrum of the ideal lattice is

$$\omega_0^2(\mathbf{k}) = \frac{1}{m_s}\sum_{\mathbf{n}} \alpha(\mathbf{n})\, e^{-i\mathbf{k}\mathbf{l}_\mathbf{n}}. \tag{7.71}$$

When the lattice has the inversion symmetry, $\alpha(\mathbf{n}) = \alpha(-\mathbf{n})$, Eq. (7.71) may be rewritten as

$$\omega_0^2(\mathbf{k}) = \frac{1}{m_s} \sum_{\mathbf{n}} \alpha(\mathbf{n}) \left[\cos \mathbf{k} \mathbf{l}_{\mathbf{n}} - 1\right]. \tag{7.72}$$

Introducing the phonon creation and annihilation operators,

$$u_{\mathbf{n}} = \sum_{\mathbf{k}} \left(\hbar/2m_s N \omega_0(\mathbf{k})\right)^{1/2} a_{\mathbf{k}}\, e^{i\mathbf{k}\mathbf{l}_{\mathbf{n}}} + \text{h.c.}\,, \tag{7.73}$$

the system Hamiltonian takes the standard form:

$$H = \sum_{\mathbf{k}} \hbar\omega_0(\mathbf{k}) \left(a_{\mathbf{k}}^* a_{\mathbf{k}} + \frac{1}{2}\right). \tag{7.74}$$

The Green functions of the ideal lattice are the following:

$$\mathcal{G}_0^c(t>0; \mathbf{n}_1, \mathbf{n}_2) = \sum_{\mathbf{k}} \left(2Ni\omega_0(\mathbf{k})\right)^{-1} \exp\left[i\mathbf{k}\left(\mathbf{l}_{\mathbf{n}_1} - \mathbf{l}_{\mathbf{n}_2}\right) - i\omega_0(\mathbf{k})\,t\right], \tag{7.75}$$

$$\mathcal{G}_0^c(t<0; \mathbf{n}_1, \mathbf{n}_2) = \sum_{\mathbf{k}} \left(2Ni\omega_0(\mathbf{k})\right)^{-1} \exp\left[-i\mathbf{k}\left(\mathbf{l}_{\mathbf{n}_1} - \mathbf{l}_{\mathbf{n}_2}\right) + i\omega_0(\mathbf{k})\,t\right], \tag{7.76}$$

and

$$\begin{aligned}\mathcal{G}_0^c(\omega; \mathbf{n}_1, \mathbf{n}_2) &= \left\{\frac{1}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}\left(\mathbf{l}_{\mathbf{n}_1} - \mathbf{l}_{\mathbf{n}_2}\right)}\right\} \left\{\frac{1}{2\omega_0(\mathbf{k})}\left[\frac{1}{\omega - \omega_0(\mathbf{k}) + i\delta} - \frac{1}{\omega + \omega_0(\mathbf{k}) - i\delta}\right]\right\} \\ &= \frac{1}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}\left(\mathbf{l}_{\mathbf{n}_1} - \mathbf{l}_{\mathbf{n}_2}\right)} \frac{1}{\omega^2 - \omega_0^2(\mathbf{k}) + i\delta}\,. \end{aligned} \tag{7.77}$$

7.6.1 One-dimensional chain

For the infinite linear chain of atoms with the interaction of nearest neighbors (NN) only, we have $\alpha(n,n) = -2\alpha(n, n \pm 1)$ [recall that $\sum_n \alpha(n) = 0$]. Thus, from (8.14) we obtain the following spectrum of the chain,

$$\omega_0^2(k) = \omega_m^2 \sin^2(ak/2)\,, \tag{7.78}$$

where $\omega_m^2 = 4\alpha/m_s$ and $\alpha = \alpha(0)/2$. Then,

$$\mathcal{G}_0^c(\omega; k) = \frac{1}{\omega^2 - \omega_0^2(k) + i\delta}\,, \tag{7.79}$$

and the spatial Fourier transform is defined as

$$\mathcal{G}_0^c(\omega; n) = \frac{1}{N}\sum_k e^{ikl_n} \mathcal{G}_0^c(\omega; k)\,, \quad \mathcal{G}_0^c(\omega; k) = \sum_n e^{-ikl_n} \mathcal{G}_0^c(\omega; n)\,. \tag{7.80}$$

Thus, we have for the 1D system (let $a = 1$ in what follows)

$$\begin{aligned}\mathcal{G}_0^c(\omega; n) &= \frac{1}{2\pi}\int_{-\pi}^{+\pi} dk\, e^{ikn} \frac{1}{\omega^2 - \omega_0^2(k) + i\delta} \\ &= \left(\frac{2}{\omega_m^2}\right)(-i)(-1)^{|n|} \frac{1}{\sqrt{1-x^2}} \left(x - i\sqrt{1-x^2}\right)^{|n|}, \end{aligned} \tag{7.81}$$

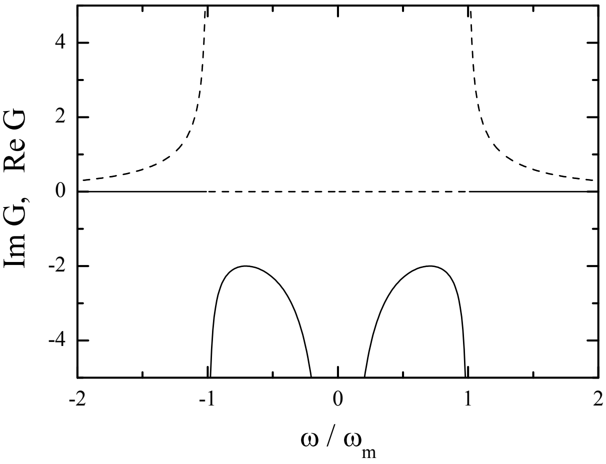


Figure 7.1: Green function for one-dimensional chain: Im (solid curve) and Real (dash curve) (multiplied by ω_m^2).

where

$$x = \left(\omega^2 - \frac{1}{2}\omega_m^2\right) \Big/ \left(\frac{1}{2}\omega_m^2\right) \tag{7.82}$$

and

$$\sqrt{1-x^2} = 2\left|\frac{\omega}{\omega_m}\right|\sqrt{1-\left(\frac{\omega}{\omega_m}\right)^2}, \tag{7.83}$$

so that $|x| < 1$ inside the phonon zone, and $1 < x < +\infty$ outside it. Outside of the phonon zone, $|\omega| > \omega_m$, when $|x| > 1$, we have to take

$$\sqrt{1-x^2} = -i\,\mathrm{sign}(x)\,\sqrt{x^2-1}\,. \tag{7.84}$$

The Green function for the one-dimensional chain is shown in Fig. 7.1.

The density of states of the chain is ($\epsilon = \omega^2$)

$$g_0(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathcal{G}_0^c(\omega;0) = \frac{1}{\pi}\frac{1}{\sqrt{\epsilon(\omega_m^2-\epsilon)}}\,, \tag{7.85}$$

$$\rho(\omega) = \frac{2}{\pi}N\frac{1}{\sqrt{\omega_m^2-\omega^2}}\,. \tag{7.86}$$

The function $g_0(\epsilon)$ is shown in Fig. 7.2.

7.6.2 Two-dimensional lattice

...

7.6.3 Three-dimensional crystal

Using a general approach (not connected with a particular symmetry of the 3D lattice), one may show (e.g., see []) that at the bottom of the acoustic phonon zone the density of phonon states behaves as

$$\rho(\omega) \propto \omega^2, \quad g(\epsilon) \propto \sqrt{\epsilon}\,. \tag{7.87}$$

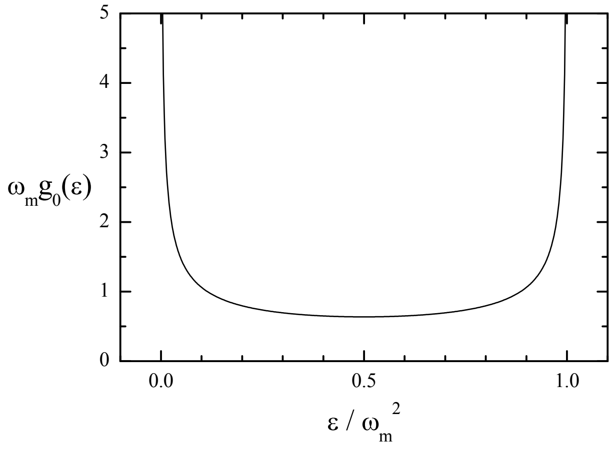


Figure 7.2: Local density of phonon states for one-dimensional chain.

Near other zone boundaries, e.g. at the top of the acoustic zone, the phonon density has root-type peculiarities,

$$\rho(\omega) \propto \sqrt{\omega_m - \omega}\,, \quad g(\epsilon) \propto \sqrt{\omega_m^2 - \epsilon}\,. \tag{7.88}$$

Besides, topology reasons in the 3D case result in at least (?) two van-Hove (root-type) peculiarities in a middle of every zone.

Debye model

In the simplest approximation, the phonon spectrum is assumed to be acoustic for all k,

$$\omega_0^2(\mathbf{k}) = (sk)^2, \tag{7.89}$$

where s is the sound velocity, and also one assumes that the spectrum is artificially cut at the maximum wavevector q_D which is determined by the ...

$$q_D^3 = (2\pi)^3 \left(\frac{4}{3}\pi\Omega_0\right)^{-1}, \tag{7.90}$$

where $\Omega_0 = V/N$ is the volume of the simple elementary cell. Thus, the maximum phonon frequency is $\omega_m = sq_D$, or

$$\omega_m^3 = 6\pi^2 s^3/\Omega_0\,. \tag{7.91}$$

The sum over k in the isotropic system is reduces to

$$\frac{1}{N}\sum_k \ldots = \frac{\Omega_0}{(2\pi)^3} 4\pi \int_0^{q_D} dk\, k^2 \ldots \tag{7.92}$$

Additionally, we have to introduce the factor of 3 due to summation over three phonon modes. Thus, the Green function is defined by the integral

$$\mathcal{G}_0^c(0) = \frac{4\pi\Omega_0}{(2\pi s)^3} \int_0^{sq_D} du\, \frac{u^2}{\omega^2 - u^2 + i\delta}\,, \tag{7.93}$$

which gives

$$\operatorname{Im}\mathcal{G}_0^c(0) = -\frac{\Omega_0}{4\pi s^3}|\omega| \quad \text{if} \quad |\omega| < \omega_m \tag{7.94}$$

and $\operatorname{Im}\mathcal{G}_0^c(0) = 0$ outside the zone,

$$\operatorname{Re}\mathcal{G}_0^c(0) = \frac{\Omega_0}{2\pi^2 s^3}\left[\frac{\omega}{2}\ln\left|\frac{\omega+\omega_m}{\omega-\omega_m}\right| - \omega_m\right], \tag{7.95}$$

so that $\operatorname{Re}\mathcal{G}_0^c(0) \approx \omega^{-2}$ at $\omega \to \infty$.

Simple cubic lattice

For the 3D crystal with a simple cubic lattice and interaction of nearest neighbors only, we have $\sum_n \alpha(n) = \alpha(0) + 6\,\alpha(1) = 0$, so that the phonon spectrum takes the following form,

$$\omega_0^2(\mathbf{k}) = \frac{1}{3}\,\omega_m^2\left[\sin^2(ak_x/2) + \sin^2(ak_y/2) + \sin^2(ak_z/2)\right], \tag{7.96}$$

where $\omega_m^2 = 2\alpha(0)/m_s$.

In the long-wave (low-frequency) limit, $|k| \ll \pi/a$, the spectrum reduces to

$$\omega_0^2(\mathbf{k}) \approx s^2k^2, \tag{7.97}$$

where $s = a\omega_m/2\sqrt{3}$ is the sound velocity.

To find the local density of states analogously to the 1D case, we have to substitute $\omega_m^2 \to \frac{1}{3}\,\omega_m^2$ and $\omega^2 \to \omega^2 - \frac{1}{3}\,\omega_m^2[\sin^2(k_1/2)+\sin^2(k_2/2)]$ in the expressions (8.14), and to take additionally the integral $(2\pi)^{-2}\int\int_{-\pi}^{+\pi} dk_1\, dk_2 \ldots$ This can be done analytically near the zone boundaries only. At the bottom of the phonon zone, $\omega \sim 0$, we have $x = -1 + y$, $y \approx 6\omega^2/\omega_m^2 - (k_1^2 + k_2^2)/2$, thus obtaining

$$\operatorname{Im}\mathcal{G}_0^c(0) \approx -\frac{6\sqrt{3}}{\pi}\frac{1}{\omega_m^3}|\omega|\,. \tag{7.98}$$

Close to the top of phonon zone, $\omega \sim \omega_m$, we may change the integration variable, $k \to q = \pi - k$, so that $x = 1 - y$, $y \approx \left[6(\omega_m^2 - \omega^2)/\omega_m^2\right] - q^2$, and we obtain

$$\operatorname{Im}\mathcal{G}_0^c(0) \approx -\frac{3\sqrt{3}}{\pi}\frac{1}{\omega_m^3}\sqrt{\omega_m^2 - \omega^2}\,. \tag{7.99}$$

Note that the density of states has a root-type peculiarity at the top boundary.

7.7 Dyson Equation

The main advantage of using the Green function technique is that we may use the procedure of *sequent incorporation of perturbations.* Namely, if two systems are characterized by different matrices $\mathbf{D}_0$ and $\mathbf{D}$,

$$(\omega^2\mathbf{1} - \mathbf{D}_0)\,\mathcal{G}^{\mathbf{c}}{}_0 = \mathbf{1} \quad\text{and}\quad (\omega^2\mathbf{1} - \mathbf{D})\,\mathcal{G}^{\mathbf{c}} = \mathbf{1}\,, \tag{7.100}$$

then their Green functions are coupled by the Dyson equation

$$\mathcal{G}^c = \mathcal{G}_0^c + \mathcal{G}_0^c\,\delta\mathbf{D}\,\mathcal{G}^c = \mathcal{G}_0^c + \mathcal{G}^c\,\delta\mathbf{D}\,\mathcal{G}_0^c\,, \tag{7.101}$$

where

$$\delta\mathbf{D} = \mathbf{D} - \mathbf{D}_0\,. \tag{7.102}$$

Proof:

$$(\omega^2\mathbf{1} - \mathbf{D})\,\boldsymbol{\mathcal{G}}^{\mathbf{c}} + \delta\mathbf{D}\,\boldsymbol{\mathcal{G}}^{\mathbf{c}} = \mathbf{1} + \delta\mathbf{D}\,\boldsymbol{\mathcal{G}}^{\mathbf{c}}, \tag{7.103}$$

$$(\omega^2\mathbf{1} - \mathbf{D}_0)\,\boldsymbol{\mathcal{G}}^{\mathbf{c}} = \mathbf{1} + \delta\mathbf{D}\,\boldsymbol{\mathcal{G}}^{\mathbf{c}}, \tag{7.104}$$

$$\boldsymbol{\mathcal{G}}^{\mathbf{c}} = (\omega^2\mathbf{1} - \mathbf{D}_0)^{-1}(\mathbf{1} + \delta\mathbf{D}\,\boldsymbol{\mathcal{G}}^{\mathbf{c}})\,. \tag{7.105}$$

Important note: the perturbation $\delta\mathbf{D}$ could not be small here, because *the Dyson equation is exact.*

7.8 Examples

7.8.1 Changing of one bond between the atoms

Let we change one bond between the $n = 0$ and $n = 1$ atoms in the 1D system, so that the perturbation is

$$V_{\text{new}}(x_0 - x_1) = V_{\text{old}}(x_0 - x_1) + \delta V(x_0 - x_1)\,. \tag{7.106}$$

The only nonzero α's in this case are $\alpha(0,0) = \alpha(1,1)$ and $\alpha(0,1)$. Therefore, the only nonzero perturbations are

$$\delta D(0,0) = \delta\alpha(0,0)/m_0\,, \quad \delta D(1,1) = \delta\alpha(1,1)/m_1\,, \tag{7.107}$$

$$\delta D(0,1) = \delta D(1,0) = \delta\alpha(0,1)/\sqrt{m_0 m_1}\,. \tag{7.108}$$

The Dyson equation to be solved, takes now the following form:

$$\begin{aligned}
&\{1 - \mathcal{G}_0^c(0,0)\;\delta D(0,0) - \mathcal{G}_0^c(0,1)\;\delta D(1,0)\}\,\mathcal{G}^c(0,0) \\
&= \mathcal{G}_0^c(0,0) + \{\mathcal{G}_0^c(0,0)\;\delta D(0,1) + \mathcal{G}^c(0,1)\;\delta D(1,1)\}\,\mathcal{G}^c(1,0) \\
&\times \{1 - \mathcal{G}_0^c(1,0)\;\delta D(0,1) - \mathcal{G}_0^c(1,1)\;\delta D(1,1)\}\,\mathcal{G}^c(1,0) \\
&= \mathcal{G}_0^c(1,0) + \{\mathcal{G}_0^c(1,0)\;\delta D(0,0) + \mathcal{G}_0^c(1,1)\;\delta D(1,0)\}\,\mathcal{G}^c(0,0)\,.
\end{aligned} \tag{7.109}$$

The denominator of the Green function is the same for all its elements, and it is equal to

$$\begin{aligned}
\mathcal{Z} = 1 &- \mathcal{G}_0^c(0,0)\;\delta D(0,0) - \mathcal{G}_0^c(1,1)\;\delta D(1,1) - \mathcal{G}_0^c(0,1)\;\delta D(1,0) - \mathcal{G}_0^c(1,0)\;\delta D(0,1) \\
&+ [\mathcal{G}_0^c(0,0)\mathcal{G}_0^c(1,1) - \mathcal{G}_0^c(0,1)\mathcal{G}_0^c(1,0)]\,[\delta D(0,0)\;\delta D(1,1) - \delta D(0,1)\;\delta D(1,0)]\;.
\end{aligned} \tag{7.110}$$

Defining

$$G^* = \mathcal{G}_0^c(0,0)\,\mathcal{G}_0^c(1,1) - \mathcal{G}_0^c(0,1)\,\mathcal{G}_0^c(1,0)\,, \tag{7.111}$$

different elements of the Green function matrix are given by the following expressions:

$$\begin{aligned}
\mathcal{Z}\mathcal{G}^c(0,0) &= \mathcal{G}_0^c(0,0) - G^*\delta D(1,1)\,, \\
\mathcal{Z}\mathcal{G}^c(1,1) &= \mathcal{G}_0^c(1,1) - G^*\delta D(0,0)\,, \\
\mathcal{Z}\mathcal{G}^c(1,0) &= \mathcal{G}_0^c(1,0) + G^*\delta D(1,0)\,,
\end{aligned} \tag{7.112}$$

and

$$\begin{aligned}
\mathcal{G}^c(n,0) = \mathcal{G}_0^c(n,0) &+ \{\mathcal{G}_0^c(n,0)\;\delta D(0,0) + \mathcal{G}_0^c(n,1)\;\delta D(1,0)\}\,\mathcal{G}^c(0,0) \\
&+ \{\mathcal{G}_0^c(n,0)\;\delta D(0,1) + \mathcal{G}_0^c(n,1)\;\delta D(1,1)\}\,\mathcal{G}^c(1,0)\,, \\
\mathcal{G}^c(n,1) = \mathcal{G}_0^c(n,1) &+ \{\mathcal{G}_0^c(n,0)\;\delta D(0,1) + \mathcal{G}_0^c(n,1)\;\delta D(1,1)\}\,\mathcal{G}^c(1,1) \\
&+ \{\mathcal{G}_0^c(n,0)\;\delta D(0,0) + \mathcal{G}_0^c(n,1)\;\delta D(1,0)\}\,\mathcal{G}^c(0,1)\,,
\end{aligned} \tag{7.113}$$

etc.

7.8.2 “Surface” (a broken bond)

I. M. Lifshitz [] was the first who recognized that the technique described in the previous subsection, may be used to describe a surface of a crystal. Indeed, if we cut the bond between the 0-th and 1-th atoms, we obtain two semi-infinite chains, each having one “free” end.

When the bond 0–1 of the ideal chain is broken, we have $V^{(0)}(x_0 - x_1) = \frac{1}{2}\alpha(u_0 - u_1)^2$ and $V(x_0 - x_1) = 0$, so that the perturbation is $\Delta V(x_0 - x_1) = -\frac{1}{2}\,\alpha(u_0 - u_1)^2$. Thus, the nonzero α's are

$$\delta\alpha(0,0) = \delta\alpha(1,1) = -\delta\alpha(0,1) = -\delta\alpha(1,0) = -\alpha\,, \tag{7.114}$$

and the nonzero elements of the matrix $\delta D(\ldots) = \delta\alpha(\ldots)/m_s$ are the following,

$$\delta D(0,0) = \delta D(1,1) = -\delta D(0,1) = -\delta D(1,0) = -\alpha/m_s = -\omega_m^2/4\,. \tag{7.115}$$

Then, an idea is that because the bond 0–1 is broken, we have $\mathcal{G}^c(1,0) = 0$. But because of $\mathcal{G}^c(1,0) \propto \mathcal{G}_0^c(1) - G^*\delta D(0,0)$, it follows that $G^*\delta D(0,0) = \mathcal{G}_0^c(1)$. Now, using

$$\mathcal{G}_0^c(0) - \mathcal{G}_0^c(1) = \left(\frac{2}{\omega_m^2}\right)(-i)\,\frac{1 + x - i\sqrt{1-x^2}}{\sqrt{1-x^2}}\,, \tag{7.116}$$

we obtain for the denominator of the Green function the expression

$$\mathcal{Z} = 1 - 2\,\delta D(0,0)\,[\mathcal{G}_0^c(0) - \mathcal{G}_0^c(1)] = -i(1+x)/\sqrt{1-x^2}\,. \tag{7.117}$$

Also, because of $\mathcal{Z}\mathcal{G}^c(1,1) = \mathcal{G}_0^c(0) - \mathcal{G}_0^c(1)$, we have for the “surface” Green function

$$\mathcal{G}^c(1,1) = \left(\frac{2}{\omega_m^2}\right)\frac{1 + x - i\sqrt{1-x^2}}{1+x}\,. \tag{7.118}$$

Thus, the “surface” spectrum is

$$g_{11}(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathcal{G}^c(1,1) = \frac{2}{\pi\omega_m^2}\sqrt{\frac{1-x}{1+x}} = \frac{2}{\pi\omega_m^2}\frac{\sqrt{\omega_m^2-\omega^2}}{\omega}\,, \tag{7.119}$$

and

$$\nu_{11}(\omega) \propto \omega\, g_{11}(\omega) \propto \sqrt{\omega_m^2 - \omega^2}\,. \tag{7.120}$$

The function (8.14) is shown in Fig. 7.3.

Returning to the ω variable, we have for the “surface” Green function the following expression:

$$\mathrm{Im}\,\mathcal{G}_s^c(\omega;0,0) = \begin{cases} -\frac{2}{\omega_m^2}\frac{\sqrt{\omega_m^2-\omega^2}}{|\omega|} & \text{inside the zone,}\quad |\omega| \le \omega_m, \\ 0 & \text{outside of the zone,}\quad |\omega| > \omega_m, \end{cases} \tag{7.121}$$

$$\mathrm{Re}\,\mathcal{G}_s^c(\omega;0,0) = \begin{cases} \frac{2}{\omega_m^2} = \text{Const} & \text{inside the zone,}\quad |\omega| \le \omega_m, \\ \frac{2}{\omega_m^2}\left(1 - \sqrt{\frac{x-1}{x+1}}\right) & \text{outside of the zone,}\quad |\omega| > \omega_m. \end{cases} \tag{7.122}$$

The surface Green function $\mathcal{G}_s^c(\omega;0,0)$ is plotted in Fig. 7.4.

The technique described above, was used in a number of studies devoted to surface physics. The technique may easily be generalized for the 2D and 3D cases, if the splitting of the crystal into two semi-infinite parts can be done by cutting only the bonds between the “surface” atoms of these two parts (fig: ... can ... cannot). These may be done for the (100) ... surfaces of simple cubic, f.c.c., b.c.c. crystals. In other cases, this technique becomes essentially useless.

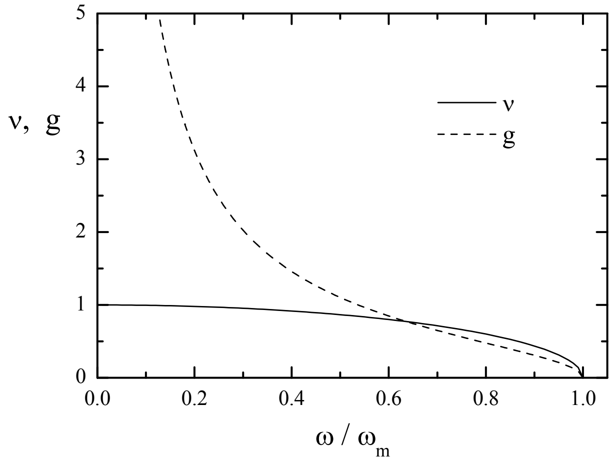


Figure 7.3: “Surface” local density of phonon states in one-dimensional semi-infinite chain.

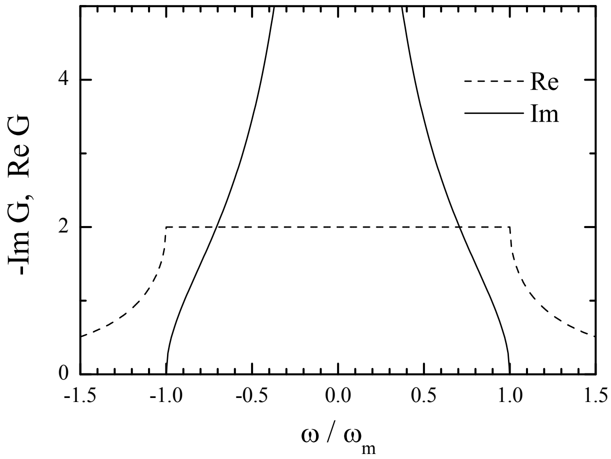


Figure 7.4: “Surface” phonon Green function”.

In particular, for the (100) surface of the 3D simple cubic lattice, repeating the calculations described above in Sec. 8.14, for the local surface Green function we obtain near the zone bottom, $\omega \sim 0$,

$$\mathrm{Im}\,\mathcal{G}_s^c(\omega;0) \approx -\frac{12\sqrt{3}}{\pi}\frac{1}{\omega_m^3}|\omega|\,, \tag{7.123}$$

and close to the top of phonon zone, $\omega \sim \omega_m$,

$$\mathrm{Im}\,\mathcal{G}_s^c(\omega;0) \approx -\frac{6\sqrt{3}}{\pi}\frac{1}{\omega_m^5}(\omega_m^2-\omega^2)^{3/2}. \tag{7.124}$$

Note that the peculiarity of the "surface" local density of phonon states (7.124) at the top boundary is different from that in the bulk of the crystal.

In model calculations where the surface phonon spectrum is used, the surface phonon Green function may be approximated by the function

$$\mathrm{Im}\,\mathcal{G}_s^c(0) = -\frac{16}{\omega_m^6}|\omega|(\omega_m^2-\omega^2)^{3/2}. \tag{7.125}$$

The function (7.125) is normalized by the condition $\pi^{-1}\int_0^{\omega_m^2} d(\omega^2)\ \{-\mathrm{Im}\,\mathcal{G}_s^c(\omega;0)\} = 1$, and also it correctly describes the behavior near the zone boundaries. The real part of the phonon function in this case may be determined by the Kramers-Kronig relation,

$$\mathrm{Re}\,\mathcal{G}_s^c(\omega;0) = \frac{32}{\pi\omega_m^2} f\left(\frac{\omega}{\omega_m}\right), \tag{7.126}$$

where

$$f(\xi) = \mathcal{P}\int_0^1 dt\ \frac{t^2(1-t^2)^{3/2}}{\xi^2-t^2}\,, \tag{7.127}$$

so that $f(1) = \pi/16$ and $f(0) = -3\pi/16$.

7.8.3 A mass impurity in the chain

Let a mass of one of atoms in the chain, say the atom with the number $n = 0$, is changed,

$$m_0 = m_s + \Delta m\,. \tag{7.128}$$

The nonzero perturbations in this case are:

$$\delta D(0,0) = \alpha(0,0)\left(\frac{1}{m_0}-\frac{1}{m_s}\right),$$

$$\delta D(n,0) = \delta D(0,n) = \alpha(n,0)\left(\frac{1}{\sqrt{m_0 m_s}}-\frac{1}{m_s}\right), \quad n \neq 0. \tag{7.129}$$

The Dyson equation takes the following form,

$$\left[1-\mathcal{G}_0^c(0,0)\ \delta D(0,0)-\sum_{n\neq 0}\mathcal{G}_0^c(0,n)\ \delta D(n,0)\right]\ \mathcal{G}^c(0,0)$$
$$= \mathcal{G}_0^c(0,0)+\sum_{n\neq 0}\mathcal{G}_0^c(0,0)\ \delta D(0,n)\ \mathcal{G}^c(n,0)\,, \tag{7.130}$$

$$\mathcal{G}^c(n,0)=\mathcal{G}_0^c(n,0)+\left[\mathcal{G}_0^c(n,0)\;\delta D(0,0)+\sum_{n_1\neq 0}\mathcal{G}_0^c(n,n_1)\;\delta D(n_1,0)\right]\;\mathcal{G}^c(0,0)$$
$$+\sum_{n_1\neq 0}\mathcal{G}_0^c(n,0)\;\delta D(0,n_1)\;\mathcal{G}^c(n_1,0)\,. \tag{7.131}$$

After long but straightforward calculations we obtain finally in this case:

$$\mathcal{Z}\mathcal{G}^c(0,0)=\mathcal{G}_0^c(0,0)\,, \tag{7.132}$$

$$\mathcal{Z}\mathcal{G}^c(n,0)=\mathcal{G}_0^c(n,0)+\sum_{n_1\neq 0}\left[\mathcal{G}_0^c(0,0)\,\mathcal{G}_0^c(n,n_1)-\mathcal{G}_0^c(n,0)\,\mathcal{G}_0^c(0,n_1)\right]\,\delta D(n_1,0)\,, \tag{7.133}$$

where the denominator $\mathcal{Z}$ is equal to

$$\mathcal{Z}=1-\mathcal{G}_0^c(0,0)\;\delta D(0,0)-\sum_{n\neq 0}[\delta D(0,n)\;\mathcal{G}_0^c(n,0)+\mathcal{G}_0^c(0,n)\;\delta D(n,0)]$$
$$-\sum_{n\neq 0}\sum_{n_1\neq 0}\delta D(0,n)\;[\mathcal{G}_0^c(0,0)\,\mathcal{G}_0^c(n,n_1)-\mathcal{G}_0^c(n,0)\,\mathcal{G}_0^c(0,n_1)]\;\delta D(n_1,0)\,. \tag{7.134}$$

Mass impurity in the ideal chain

When the mass of the atom with the number $n=0$ is changed in the ideal chain, we have $\delta D(0,0)=-\alpha(0)\;\Delta m/m_0 m_s$ and $\delta D(n,0)=\alpha(n)\left(\sqrt{\frac{m_s}{m_0}}-1\right)\Big/m_s$. Using ... , we obtain

$$\mathcal{Z}=\frac{m_s}{m_0}\left[1+\omega^2\mathcal{G}_0^c(0,0)\frac{\Delta m}{m_s}\right]. \tag{7.135}$$

As is known, the equation

$$\mathrm{Re}\;\mathcal{Z}=0 \tag{7.136}$$

determines the frequencies of phonon states. Presenting the real part of the Green function as

$$\mathrm{Re}\,\mathcal{G}_0^c(\epsilon;0,0)=\mathrm{Re}\,\frac{1}{N}\sum_k\frac{1}{\epsilon-\omega_0^2(k)}=\int d\epsilon'\;g_0(\epsilon')\frac{1}{\epsilon-\epsilon'}\,, \tag{7.137}$$

equation (7.130) may be rewritten as

$$F(\epsilon)=-\frac{m_s}{\Delta m}\,,\quad\text{where}\quad F(\epsilon)=\epsilon\int_0^{\omega_m^2}d\epsilon'\;\frac{g_0(\epsilon')}{\epsilon-\epsilon'}\,. \tag{7.138}$$

Note that $F(\epsilon)>F(\infty)=1$ (?).

In the case of the acoustical phonon zone, Eq. (7.138) has a solution outside the zone at $\omega=\omega_{\rm loc}>\omega_m$ (the high-frequency mode) if and only if the impurity atom is light, $\Delta m<0$, and, moreover, if

$$\Delta m<-m_s/F(\omega_m^2)\,. \tag{7.139}$$

When the spectrum has also an optical branch, a local mode may split out from the top of zone (if the impurity is light), or it may split out from the bottom of the optical zone (for a heavy impurity). The amplitude of local vibrations as a function of the distance from the impurity atom decays exponentially, $u_n\propto\exp(-n/a_{\rm loc})$, where

$$a_{\rm loc}\approx\left(\frac{\omega_{\max}-\omega_{\min}}{\omega_{\rm loc}-\omega_{\max/\min}}\right)^{1/2}. \tag{7.140}$$

7.8.4 Adsorbed atom

Let we have separately a substrate and a free atom, and let $|\mathrm{A}\rangle$ be the wavefunction of the atom, and $|0\rangle$ be the wavefunction of the adcenter. The Green function of the free atom is $\mathcal{G}^{(0)}(\omega;A,A)=(\omega^2+i\delta)^{-1}$. Let we know also the Green function of the substrate: $\mathcal{G}_s(\omega)\equiv\mathcal{G}^{(0)}(\omega;0,0)$. When the atom and the substrate are not coupled, we have $\mathcal{G}^{(0)}(\omega;A,0)=\mathcal{G}^{(0)}(\omega;0,A)=0$.

Now let the atom and the substrate became coupled by the potential $V(x_A-x_0)$. This potential produces the perturbation

$$\Delta\alpha(0,0)=\Delta\alpha(A,A)=-\Delta\alpha(A,0)=-\Delta\alpha(0,A)=\left.\frac{d^2V(u)}{du^2}\right|_{u=u^{(0)}}\equiv\Delta\alpha\,. \tag{7.141}$$

Denoting by m_A the mass of the adatom, and by m_s, the mass of the substrate atoms, for the nonzero elements of the matrix $\delta\mathbf{D}$ we obtain

$$\delta D(0,0)=\Delta\alpha/m_s\,,\quad \delta D(A,A)=\Delta\alpha/m_A\,,\quad \delta D(A,0)=\delta D(0,A)=-\Delta\alpha/\sqrt{m_s m_A}\,. \tag{7.142}$$

The denominator of the Green function in this case is given by the following expression,

$$\mathcal{Z}=1-\mathcal{G}_s(\omega)\left(\frac{\Delta\alpha}{m_s}\right)-\frac{1}{\omega^2+i\delta}\left(\frac{\Delta\alpha}{m_A}\right). \tag{7.143}$$

The function $\mathcal{Z}(\omega)$ has poles at the frequencies which are solutions of the equation

$$\omega^2=\left(\omega_A^{(0)}\right)^2\left\{1+\frac{m_A}{m_s}\,\omega^2\,\mathcal{G}_s(\omega)\right\}, \tag{7.144}$$

where $\omega_A^{(0)}=\sqrt{\Delta\alpha/m_A}$ is the frequency of adatom vibrations on the rigid substrate (i.e. in the limit $m_s\to\infty$).

Let us define now ω_0 and δ_0 by the equations

$$\omega_0^2=\left(\frac{\Delta\alpha}{m_A}\right)\left\{1+\frac{m_A}{m_s}\,\omega_0^2\;\mathrm{Re}\,\mathcal{G}_s(\omega_0)\right\} \tag{7.145}$$

and

$$\delta_0^2=-\left(\frac{\Delta\alpha}{m_s}\right)\omega_0^2\;\mathrm{Im}\,\mathcal{G}_s(\omega_0)>0\,. \tag{7.146}$$

Now one can see that the coupling (8.14) results in the destroying the zero-frequency pole corresponded to the free atom, and the emerging of a new pole characterized by the frequency

$$\omega_A=\left(\omega_0^4+\delta_0^4\right)^{1/4}\cos(\phi)\approx\omega_0 \tag{7.147}$$

and the half-width at the half-peak (HWH?)

$$\gamma_A=\left(\omega_0^4+\delta_0^4\right)^{1/4}\sin(\phi)\approx\delta_0^2/2\omega_0\,, \tag{7.148}$$

where

$$\phi=\frac{1}{2}\tan^{-1}\left(\delta_0^2/\omega_0^2\right). \tag{7.149}$$

Thus, if ω_A lies within the zone of the substrate phonons, we have the *quasilocal* (*virtual*) vibration,

$$\mathcal{G}^{\mathbf{c}}(t)\propto e^{i\omega_A t-\gamma_A t}. \tag{7.150}$$

Otherwise, when ω_A lies outside of the phonon zone, the vibration is *local*.

The Green functions themselves in this case are the following:

$$\mathcal{G}^{\mathbf{c}}(\omega; A, A) = \left[1 - \frac{\Delta\alpha}{m_s}\right] \Big/ \mathcal{Z}_A(\omega)\,, \tag{7.151}$$

$$\mathcal{G}^{\mathbf{c}}(\omega; 0, 0) = \mathcal{G}_s(\omega) \left[\omega^2 - \frac{\Delta\alpha}{m_A}\right] \Big/ \mathcal{Z}_A(\omega)\,, \tag{7.152}$$

and

$$\mathcal{G}^{\mathbf{c}}(\omega; A, 0) = -\frac{\Delta\alpha}{\sqrt{m_A m_s}}\, \mathcal{G}_s(\omega) \Big/ \mathcal{Z}_A(\omega)\,, \tag{7.153}$$

where

$$\mathcal{Z}_A(\omega) = \omega^2 - \frac{\Delta\alpha}{m_A} \left[1 + \frac{m_A}{m_s}\, \omega^2\, \mathcal{G}_s(\omega)\right]. \tag{7.154}$$

Notice also that

$$\left(1 + \frac{m_A}{m_s}\right) \Big/ m_A = \frac{m_s + m_A}{m_s m_A} = \frac{1}{m_{\text{reduced}}}\,. \tag{7.155}$$

Chapter 8

Diagram Technique

...

8.1 Perturbation Series

The perturbation theory for interacting particles is based on the dynamical perturbation theory described above in Sec. 8.14.

It is convenient to introduce the operator

$$S'_\delta \equiv S(+\infty, -\infty) = S(+\infty, 0) S(0, -\infty)\,. \tag{8.1}$$

Because for the perturbation (8.14) we have $S(0, -\infty) = S(0, +\infty)$, Eqs. (8.14) may simply be rewritten in terms of S'_δ:

$$|\Psi_0\rangle = \frac{S_\delta |\Phi_0\rangle}{\left[\langle \Phi_0 | S'_\delta | \Phi_0 \rangle\right]^{1/2}} \tag{8.2}$$

and

$$\Delta E = \frac{1}{2} \lim_{\delta \to +0} i\hbar\delta g \frac{\partial}{\partial g} \ln \langle \Phi_0 | S'_\delta | \Phi_0 \rangle\,. \tag{8.3}$$

Besides, analogously we can obtain the expression for the $T = 0$ causal Green function,

$$\langle\langle A(t) | B(t') \rangle\rangle = \frac{1}{i} \frac{\langle \Phi_0 | T_{\mathrm{ch}} \left[A_{\mathrm{int}}(t)\, B_{\mathrm{int}}(t')\, S'_\delta \right] | \Phi_0 \rangle}{\langle \Phi_0 | S'_\delta | \Phi_0 \rangle}\,. \tag{8.4}$$

The main trick in the diagram approach is to introduce the normal product and then to apply the Wick theorem.

The *normal product* $\mathcal{N}(AB)$ of two operators A and B is defined so that all creation operators are arranged to the left of all annihilation operators. Then, define the *pairing* as

$$\overbrace{AB} = T_{\mathrm{ch}}(AB) - \mathcal{N}(AB)\,. \tag{8.5}$$

Define also: (???)

$$\left(\sum_i A_i \right) \left(\sum_k A_k \right) = \sum_{ik} \overbrace{A_i B_k}\,, \tag{8.6}$$

$$\mathcal{N}(PQRST \ldots XYZ) = \eta^P\, \overbrace{QS}\, \overbrace{RY}\, \mathcal{N}(PT \ldots XZ)\,. \tag{8.7}$$

Then, the Wick theorem says that

$$T_{\text{ch}}(A_1A_2\dots A_n) = \mathcal{N}(A_1A_2\dots A_n) + \mathcal{N}(\overbrace{A_1A_2}\dots A_n) + \dots + \text{all paired}. \tag{8.8}$$

Then the main idea is that $\langle\Phi_0|\mathcal{N}(A_1A_2\dots A_n)|\Phi_0\rangle \neq 0$, only if all operators are paired, because otherwise an annihilation operator acts on $|\Phi_0\rangle$ and gives zero. Finally, we get that $\langle\Phi_0|T_{\text{ch}}(A_1A_2\dots A_n)|\Phi_0\rangle$ is equal to the sum of all *completely* paired terms. Because the pairing is connected with Green functions, we obtain diagram rules. Then, from topology consideration one can show that if one uses only the connected diagrams, the logarithm in Eq. (8.14) and denominator in Eq. (8.14) both go out being cancelled:

$$\Delta E = \frac{1}{2}\lim_{\delta\to+0} i\hbar\delta g\frac{\partial}{\partial g}\langle\Phi_0|S'_\delta|\Phi_0\rangle_{\text{connected}}, \tag{8.9}$$

$$\langle\!\langle A(t)|B(t')\rangle\!\rangle = \frac{1}{i}\langle\Phi_0|T_{\text{ch}}\left[A_{\text{int}}(t)B_{\text{int}}(t')S'_\delta\right]|\Phi_0\rangle_{\text{connected}}. \tag{8.10}$$

The main advantage of the diagram perturbation theory is that the sum is over intermediate virtual particles instead of over intermediate states; this reduces the number of terms in $n!$ times. Below we consider the diagram technique for Green functions only. The perturbation series for the causal $T = 0$ Green function (either Bose or Fermi) is

$$G(t) = \underbrace{\left(\frac{1}{i}\right)}_{a}\sum_{n=0}^{\infty}\underbrace{\left(\frac{1}{n!}\right)}_{b}\underbrace{\int_{-\infty}^{+\infty}dt_1\dots\int_{-\infty}^{+\infty}dt_n}_{c}$$

$$\times\langle 0|T_{\text{ch}}\left\{\underbrace{(AB)}_{d}\underbrace{[-iH_{\text{int}}(t_1)]\dots[-iH_{\text{int}}(t_n)]}_{e}\right\}|0\rangle\,, \tag{8.11}$$

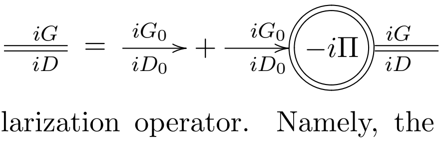
and the technique described above leads to the following diagram rules, following letters in Eq. (8.11):
(a) is the general factor for the Green function (for the polarization operator it is absent);
(b) this factor is absent when only topologically inequivalent diagrams are considered;
(c) or $\mathcal{P}\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}$ after Fourier transform; for the loop we have to integrate along the O_- contour;
(d) corresponds to the external lines (they are absent for the polarization operator);
(e) the vortices give the factors $(-iV_{\dots})$, and the lines give the factors $iG_{\dots}$ or $iD_{\dots}/\sqrt{mm}$.

The standard rules are:
− energy should be conserved in the vortices,
− Fermi loops give the factor "−1" each,
− lines should be labelled, and then one has to sum over all free indexes.

The Dyson equation is valid for any Green function:

$$G = G_0 + G_0\Pi G, \tag{8.12}$$

or



where Π is the irreducible polarization operator. Namely, the *polarization operator* (called also as the self-energy part) is the diagram without external lines, which can be inserted into the (Fermion) line; and the *irreducible* polarization operator is the polarization operator which cannot be split into two unconnected parts by removing of one (Fermion) line.

For the $T \neq 0$ Matsubara Green functions, the diagram technique is ($\beta_0 = 1/T$):

$$\mathcal{G}(\beta) = \underbrace{(-1)}_{a} \sum_{n=0}^{\infty} \underbrace{\left(\frac{1}{n!}\right)}_{b} \underbrace{\int_0^{\beta_0} d\beta_1 \ldots \int_0^{\beta_0} d\beta_n}_{c}$$

$$\times \langle 0 | T_m \left\{ \underbrace{[A^m(\beta) B^m(0)]}_{d} \underbrace{[-H_{\text{int}}(\beta_1)] \ldots [-H_{\text{int}}(\beta_n)]}_{e} \right\} |0\rangle \,, \tag{8.13}$$

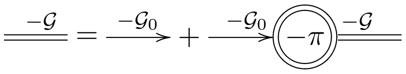
and the rules now are the following:
(a) is the general factor for the Green function (for the polarization operator it is absent);
(b) this factor is absent when only topologically inequivalent diagrams are considered;
(c) or $T\sum$ over the frequencies;
(d) the external lines (absent if the polarization operator is calculated);
(e) the vortices give the factors $(-V_{\ldots})$, and the lines give the factors $-G_{\ldots}$ or $-D_{\ldots}/\sqrt{mm}$.

The standard rules are the same as above.

The Dyson equation is:

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \pi \mathcal{G}, \tag{8.14}$$

or

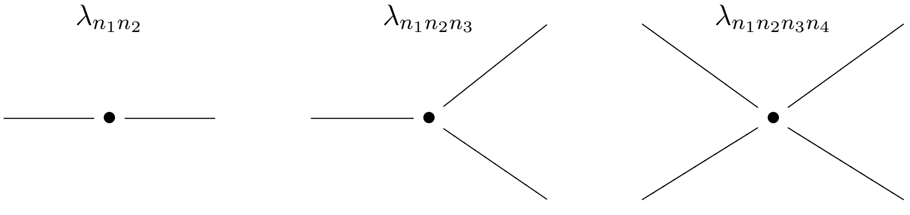


8.2 Phonon System

For the interacting phonons the Hamiltonian is

$$H_{\text{phonon}} = \frac{1}{2!} \sum_{n_1 n_2} \lambda_{n_1 n_2} u_{n_1} u_{n_2} + \frac{1}{3!} \sum_{n_1 n_2 n_3} \lambda_{n_1 n_2 n_3} u_{n_1} u_{n_2} u_{n_3} + \ldots \,, \tag{8.15}$$

and the vertices are described by the diagrams

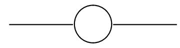


The rules of the standard diagram technique are the following:
- construct topologically nonequivalent diagrams (but only the "connected" ones – any piece of the diagram must be connected with at least one external line);
- put two indexes, e.g. n_1 and n_2, on each solid line, and then sum over these indexes, $\sum_{n_1\, n_2}$;
- associate an energy ω_i with each solid line, and the energy ω with the external lines; at vortices the energy must be conserved;
- to each solid line, put in correspondence the factor $\langle T_{\text{ch}} u_{n_1} u_{n_2} \rangle = (i/\sqrt{m_1 m_2})\, \mathcal{D}_{n_1 n_2}(\omega_i)$;
- to each vertex, put in correspondence the factor $-i\lambda_{\ldots}$;
- the factor $-i\sqrt{m_1 m_2}$ should be applied to the whole diagram (it follows from the definition of

the Green function);

- make integration over all *free* energy parameters, $\int_{-\infty}^{+\infty} d\omega_i$;
- finally, apply the Dyson equation,

$$\mathcal{D} = \mathcal{D}_0 + \mathcal{D}_0 \Pi \mathcal{D}, \tag{8.16}$$

where $\Pi =$  is the polarization diagram.

When integrating, one may use the following useful formulas:
if $\mathcal{G}_i(\omega) = \left(\omega^2 - \omega_0^2 + i0\right)^{-1}$, then

$$\int_{-\infty}^{+\infty} d\omega \; \mathcal{G}_0(\omega) = \oint_{O_+} d\omega \; \ldots = \oint_{O_-} d\omega \; \ldots = -\frac{i\pi}{\omega_0} \,, \tag{8.17}$$

so that

$$\int_{-\infty}^{+\infty} d\omega \; \mathrm{Re}\, \mathcal{G}(\omega) = 0 \,, \tag{8.18}$$

and also

$$\int_{-\infty}^{+\infty} d\omega \; \mathcal{G}_0^2(\omega) = +\frac{2\pi i}{4\omega_0^3} \,, \tag{8.19}$$

$$\int_{-\infty}^{+\infty} d\omega \; \mathcal{G}_1(\omega)\mathcal{G}_2(\omega) = +\frac{2\pi i}{2\omega_1\omega_1(\omega_1+\omega_2)} \,, \tag{8.20}$$

$$\int_{-\infty}^{+\infty} d\omega \; \mathcal{G}_1(\omega)\, \mathcal{G}_2(\omega)\, \mathcal{G}_3(\omega) = -\frac{2\pi i(\omega_1+\omega_2+\omega_3)}{2\omega_1\omega_2\omega_3(\omega_1+\omega_2)(\omega_2+\omega_3)(\omega_1+\omega_3)} \,, \tag{8.21}$$

$$\int_{-\infty}^{+\infty} d\omega \; \mathcal{G}_0^3(\omega) = -\frac{6\pi i}{16\omega_0^5} \,. \tag{8.22}$$

Besides,

$$\delta(\omega^2 - \omega_0^2) = \frac{1}{2|\omega_0|} \left[\delta(\omega - \omega_0) + \delta(\omega + \omega_0)\right]. \tag{8.23}$$

In Matsubara technique, the following trick is used:
if $h(\omega)$ is a function such that $h(\omega) \le 1/|\omega|^2$ at $\omega \to \infty$, then

$$\oint_{O_+} d\omega \; h(i\omega) f_B(\omega) = \oint_{O_-} d\omega \; h(i\omega) f_B(\omega) = -2\pi i \sum_{m=\mathrm{all}} (-T) h(\omega)_{i\omega = i(2m)\pi T} \,, \tag{8.24}$$

where O_+ is the closed circle in the clockwise direction so that it encloses the poles of $f_B(\omega)$ only, and O_- is the closed circle in the anticlockwise direction so that it encloses the poles of $h(i\omega)$ only. Therefore, for the Bose case it follows

$$T \sum_{m=-\infty}^{+\infty} \left[D^m D^m D^m \ldots\right]_{\omega_m = (2m)\pi T} = -\frac{1}{i} \oint_{\widetilde{O}_-} \frac{d\omega}{2\pi} \, f_B(\omega) D^m D^m D^m \ldots (i\omega) \,, \tag{8.25}$$

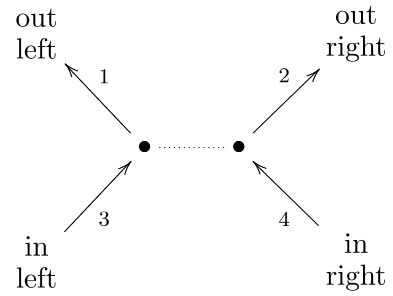
where the contour $\widetilde{O}_-$ goes out of all poles of the function $f_B(\omega)$, i.e. out of all points $\omega = i(2m)\pi T$, but encloses all poles of the function $D^m D^m D^m \ldots (i\omega)$.

8.3 Electron–Electron and Electron–Phonon Interaction

The electron-electron interaction is

$$H_{\mathrm{el-el}} = ... \; ; \tag{8.26}$$

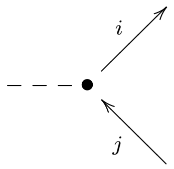
the corresponding vertex is



The electron-phonon interaction is

$$H_{\mathrm{int}} = \sum_{mij} \lambda_{mij} u_m c_i^* c_j + \ldots , \tag{8.27}$$

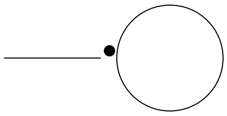
with the vertices

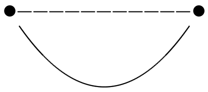


The standard diagram technique rules are now the following:

- when fermion lines (here solid lined) met at a vertex, they must preserve the direction of arrows;
- the whole diagram is multiplied by the factor $(-1)^L$, where L is the total number of Fermi loops;
- each phonon line (dashed here) corresponds to the factor $\mathcal{D} = \langle T_{\mathrm{ch}} uu \rangle$;
- the electron line $\xrightarrow{i \quad j}$ corresponds to the factor $iG_{ij}^{(0)}(\omega)$ = Fourier of $\langle T_{\mathrm{ch}} c_i(t) c_j^*(0) \rangle$ (we assume that index i incorporates spin);
- the el-ph vertex gives the factor $-i\lambda_{\ldots ij}$;
- the el-el vertex gives the factor $-iv_{1234}$;
- energy and spin must be conserved at vertices;
- make the sum over indexes (and spins);
- over free energy parameters, make $\mathcal{P} \int_{-\infty}^{+\infty} d\omega / 2\pi$.

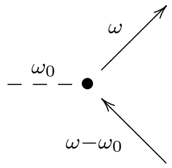
Note 1: for the two loops (and only for these two loops)





we have to use $\oint_{O_-} d\omega$, (or $t = -0$); in other cases the contour may be closed in any way (?).

Note 2: In the vertex (loop?),



where $\omega_0 > 0$, the Kramers-Kronig relation gives

$$-\int_{-\infty}^{+\infty} d\omega\, G_1(\omega)\, G_2(\omega-\omega_0) = +\int_0^{\omega_0} d\omega\, \operatorname{Im} G_1(\omega)\, \operatorname{Im} G_2(\omega-\omega_0) + (1 \Leftrightarrow 2)\,. \qquad (8.28)$$

In Matsubara technique for Fermi systems, the following trick is used: if $h(\omega)$ is a function such that $h(\omega) \leq 1/|\omega|^2$ at $\omega \to \infty$, then

$$\oint_{O_+} d\omega\, h(-i\omega) f_F(\omega) = \oint_{O_-} d\omega\, h(-i\omega) f_F(\omega) = -2\pi i \sum_{n=\mathrm{all}} (-T) h(\omega)_{i\omega=i(2n+1)\pi T}\;, \qquad (8.29)$$

where O_+ is the closed circle in the clockwise direction so that it encloses the poles of $f_F(\omega)$ only, and O_- is the closed circle in the anticlockwise direction so that it encloses the poles of $h(i\omega)$ only. Therefore, for the Fermi functions it follows

$$T \sum_{n=-\infty}^{+\infty} [G^m G^m G^m \ldots]_{\omega_n=(2n+1)\pi T} = +\frac{1}{i} \oint_{\widetilde{O}_-} \frac{d\omega}{2\pi}\, f_F(\omega) G^m G^m G^m \ldots (i\omega)\,, \qquad (8.30)$$

where the contour $\widetilde{O}_-$ goes out of all poles of the function $f_F(\omega)$, i.e. out of all points $\omega = i(2n+1)\pi T$, but encloses all poles of the function $G^m G^m G^m \ldots (i\omega)$.

Chapter 9

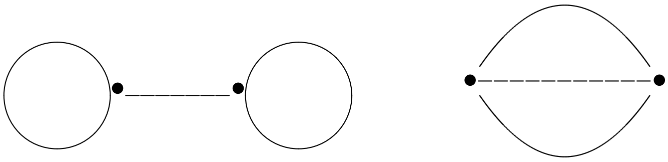
Applications

9.1 Atom He

Hamiltonian:

$$H = \sum_{\sigma} E_a n_{a\sigma} + U_a n_{a\uparrow} n_{a\downarrow} \,. \tag{9.1}$$

Diagram perturbation theory: four times the Coulomb dumb-bell plus two times the loop



give the GS energy

$$E_0 = 2E_a + U_a \,. \tag{9.2}$$

Green function technique: a Zubarev chain

$$G = \langle\langle c_{a\sigma} | c^*_{a\sigma} \rangle\rangle = \frac{1 - \overline{n}_{a,-\sigma}}{\omega - E_a} + \frac{\overline{n}_{a,-\sigma}}{\omega - E_a - U_a} \,, \tag{9.3}$$

$$\Gamma = \langle\langle c_{a\sigma} n_{a,-\sigma} | c^*_{a\sigma} \rangle\rangle = \frac{\overline{n}_{a,-\sigma}}{\omega - E_a - U_a} \,. \tag{9.4}$$

Note: this decoupling is exact (?). Self-consistency:

$$\overline{n}_{a,\sigma} = \int_{-\infty}^{\epsilon_F} d\omega \;\left[(1 - \overline{n}_{a,-\sigma})\, \delta(\omega - E_a) + (\overline{n}_{a,-\sigma})\, \delta(\omega - E_a - U_a) \right]. \tag{9.5}$$

Thus, the system has two levels at $\omega = E_a$ and $\omega = E_a + U_a$ and two electrons; therefore, both levels are occupied, $\overline{n}_{a,\sigma} = \overline{n}_{a,-\sigma} = 1$,

$$G = \Gamma = (\omega - E_a - U_a)^{-1}, \tag{9.6}$$

and the GS energy E_0 is the same.

9.2 Hubbard Model: Molecule A–B

Let us consider the molecule A–B as in Sec. 8.14, but now let us take into account the repulsion of electrons occupying the same atomic orbital. The Hamiltonian describing this system, is known as the Hubbard Hamiltonian:

$$H = \sum_\sigma \left[E_a n_{a\sigma} + E_b n_{b\sigma} + (V_{ab} c^*_{a\sigma} c_{b\sigma} + \text{h.c.})\right] + U_a n_{a\sigma} n_{a,-\sigma} + U_b n_{b\sigma} n_{b,-\sigma} \,. \tag{9.7}$$

In the Hartree-Fock approximation the electron-electron interaction term is treated as

$$n_{a\sigma} n_{a,-\sigma} \to n_{a\sigma} \overline{n}_{a,-\sigma} \,,$$

and the Green functions take the same form as in Sec. 8.14, but with the substitution

$$E_a \to \epsilon_{a\sigma} = E_a + U_a \overline{n}_{a,-\sigma} \,. \tag{9.8}$$

The dissociation energy is now equal to

$$D = U_a \overline{n}_{a\sigma} \overline{n}_{a,-\sigma} + U_b \overline{n}_{b\sigma} \overline{n}_{b,-\sigma} + E_a + E_b - \sum_\sigma \int_{-\infty}^{\epsilon_F} d\epsilon \; \epsilon \; (\rho^\sigma_a + \rho^\sigma_b) \,. \tag{9.9}$$

In particular, in the symmetric case, $E_a = E_b$ and $U_a = U_b = U$, from the symmetry reasons we may put

$$\overline{n}_{a\sigma} = \overline{n}_{b,-\sigma} = n_\sigma \,. \tag{9.10}$$

The energy levels are

$$E_{1,2} = \left(E_a + \frac{1}{2}U\right) \mp \sqrt{\frac{1}{4}U^2 \Delta n^2_\sigma + V^2} \,, \tag{9.11}$$

where

$$\Delta n_\sigma = n_\sigma - n_{-\sigma} \,. \tag{9.12}$$

When $N = 2$, then $n_\sigma + n_{-\sigma} = 1$, $E_1 < \epsilon_f < E_2$, and

$$n_\sigma = \alpha^\sigma_a = \frac{1}{2} + \frac{1}{4} \frac{U \, \Delta n_\sigma}{\sqrt{\frac{1}{4}U^2 \Delta n^2_\sigma + V^2}} \,. \tag{9.13}$$

Equation (9.13) should be solved self-consistently. At small U, when $U < 4|V|$, it has a single solution $\overline{n}_\sigma = \frac{1}{2}$, which corresponds to the dissociation energy

$$D = 2|V| - \frac{1}{2}U \,. \tag{9.14}$$

For a strong electron-electron repulsion, $U > 2|V|$, Eq. (9.13) has two solutions

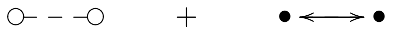
$$n_\sigma = \frac{1}{2}\left(1 \pm \sqrt{1 - \frac{4V^2}{U^2}}\right) . \tag{9.15}$$

This *magnetic* solution, when it exists, always corresponds to lower energy. The dissociation energy for the magnetic solution is

$$D = 2\frac{V^2}{U} \,. \tag{9.16}$$

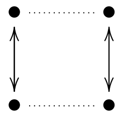
`put fig!`

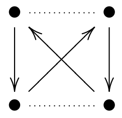
With the diagram technique, the HF GS is (4 × dumb-bell + 2 × loop)



this gives the contribution $= U$.

The second order perturbation theory is (4 × left + 2 × right)





gives the contribution $= U^2_{12ex}/(E_2 - E_1)$.

9.3 Interacting Electron Gas

9.3.1 The ground state energy

The Hamiltonian of the system of interacting electrons is

$$H = H_0 + V, \tag{9.17}$$

where H_0 was described above in Sec. 8.14, and the operator of interaction V is

$$V = \frac{1}{2}\sum_{i\neq k} v(r_i, r_k) = \frac{1}{2}\sum_{iklm} V_{iklm}\, c_i^* c_k^* c_m c_l \ , \tag{9.18}$$

$$V_{iklm} = \langle ik|v|lm\rangle = \int dr\, dr'\ v(r,r')\, \phi_i^*(r)\, \phi_k^*(r')\, \phi_l(r)\phi_m(r')\,, \tag{9.19}$$

$\phi_i(r)$ being the spin-orbitals. When the electron-electron interaction is independent of spins, we may use orbitals instead of spin-orbitals, and V takes the form

$$V = \frac{1}{2}\sum_{iklm}\sum_{\sigma\sigma'} V_{iklm}\, c_{i\sigma}^* c_{k\sigma'}^* c_{m\sigma'} c_{l\sigma} \tag{9.20}$$

$$= \frac{1}{2}\sum_{ik,\,\sigma\sigma'} \underbrace{V_{kiki}\, n_{i\sigma} n_{k\sigma'} (\text{if } i = k \text{ then } \sigma \neq \sigma')}_{\text{Coulomb repulsion}} - \frac{1}{2}\sum_{i\neq k,\,\sigma} \underbrace{V_{kiik}\, n_{i\sigma} n_{k\sigma}}_{\text{exchange}} \tag{9.21}$$

$$+\frac{1}{2}\sum_{ikm(k\neq m)}\sum_{\sigma\sigma'} V_{kimi} n_{i\sigma'} c_{k\sigma}^* c_{m\sigma} \ \ (\text{if } i = k \text{ or } i = m \text{ then } \sigma \neq \sigma') \tag{9.22}$$

$$-\frac{1}{2}\sum_{ikm,\,\sigma} V_{kiim} n_{i\sigma} c_{k\sigma}^* c_{m\sigma} \ \ (i \neq k \neq m \neq i) \tag{9.23}$$

$$+\frac{1}{2}\sum_{iklm,\,\sigma\sigma'} V_{iklm}\, c_{i\sigma}^* c_{k\sigma'}^* c_{m\sigma'} c_{l\sigma} \ \ (\text{all indexes} \neq). \tag{9.24}$$

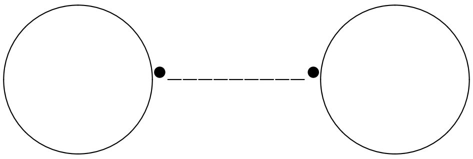
In the basis of plane waves the interaction takes the form

$$\langle k_1 k_2|v|k_3 k_4\rangle = \frac{1}{V_{\text{vol}}}\delta_{k_1+k_2,k_3+k_4} v(k_1 - k_3)\,, \tag{9.25}$$

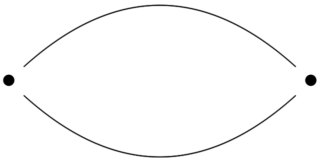
so that for the Coulomb electron-electron repulsion $v(r) = e^2/r$ we obtain

$$V = \frac{1}{2}\sum_{k_1 k_2 q}\sum_{\sigma\sigma'} V_q\, c_{k_1+q,\,\sigma}^* c_{k_2-q,\,\sigma'}^* c_{k_2,\,\sigma'} c_{k_1,\,\sigma}\ , \quad V_q = \frac{4\pi e^2}{V_{\text{vol}}}\frac{1}{q^2}\,. \tag{9.26}$$

The lowest approximation is the Hartree-Fock one. For the $T = 0$ GS the energy is determined by two diagram, the Coulomb repulsion diagram



and the exchange diagram,



The GS energy is

$$E_0^{\mathrm{HF}} = ... \tag{9.27}$$

9.3.2 Collective excitations: Plasmons

el-el interactions → plasmons: Lipkin motion equation approach
Interaction of an external charge with the electron gas: Overhauser
Diagram technique: Loop (RPA approximation)
$\epsilon(k,\omega)$ – optics
friction, conductivity, superconductivity

9.3.3 Nonzero temperature

Fermi statistics → specific heat

9.4 Interacting Phonons

The density of phonon states was described in detail in Sec. 8.14. Because phonons are Bose particles, at $T \neq 0$ they follow the Bose-Einstein statistical function f_B. Therefore, the system energy (omitting the zero phonon energy) is

$$E_0(T) = \sum_{\mathbf{k}} \hbar\omega_0(\mathbf{k}) f_B(\omega_0(\mathbf{k})) = \int d\omega\, \omega\rho(\omega) f_B(\omega)\,. \tag{9.28}$$

Thus, the average number of phonons excited at $T > 0$, is equal to

$$n = \frac{1}{V}\int d\omega\, \rho(\omega) f_B(\omega)\,, \tag{9.29}$$

and it behaves in the following way:
at $T \ll \omega_m$, for acoustical phonons $n \propto (T/\omega_m)^3$, so that $E_0(T) \sim (T/\omega_m)^3 T$, i.e. the mean energy of the phonon is T;
at $T \ll \omega_m$, for optical phonons $n \propto \exp(-\omega_{\mathrm{opt}}/T)$;
at $T \gg \omega_m$, for acoustical phonons $n \propto T$, so that $E_0(T) \sim T$ (the Dulong-Petit law), and the average phonon energy is ω_m.

...

specific heat

ph-ph interactions: phonon loop!

9.5 Electron–Phonon Interaction

9.5.1 Hamiltonian

...

9.5.2 Local polaronic model: Exact solution

... Braun and Volokitin ...

9.5.3 Variational solution

... Braun and Volokitin ...

9.5.4 Polaron

...

9.5.5 Interaction with acoustic phonons

...

9.5.6 Interaction with optical phonons

...

9.6 Impurity: Anderson Model

...

9.7 Nozieres Approach

...

9.8 Impurity: Lifetime of Local Vibrations

Recall (see Sec. 8.14): a mass of the impurity may be either lighter or heavier → the vibrations will be either localized or virtual. Now let us consider the same problem (for local vibrations), using the diagram technique

First, we obtain the old results, but in a much simpler way. Let u_a and u_s be the displacements of the adatom and the surface atom of the substrate respectively, and introduce $u = u_a - u_s$. When these atoms are isolated (does not interact), the phonon Green function is

$$\Gamma_{00}(\omega) \equiv \text{Fourier } \langle T_{\text{ch}} u(t) u(0) \rangle = \frac{i}{m_a} \frac{1}{\omega^2 + i\delta} + \frac{i}{m_s} \mathcal{D}_s \,. \tag{9.30}$$

Now, introducing the interaction $V(u)$, the interaction Hamiltonian is

$$H_{\text{int}} = \frac{1}{2!} \lambda_2 u^2 + \frac{1}{3!} \lambda_3 u^3 + \frac{1}{4!} \lambda_4 u^4 + \dots \tag{9.31}$$

In particular, for the Morse potential

$$V(u) = D\left(e^{-2\gamma u} - 2e^{-\gamma u}\right) \tag{9.32}$$

the coefficients in Eq. (9.31) are

$$\lambda_n = \frac{\partial^n}{\partial u^n} V(u) = (-1)^n 2D\gamma^n \left(2^{n-1} - 1\right), \tag{9.33}$$

so that $\lambda_2 = 2D\gamma^2 = m_a \omega_a^2$, $\lambda_3 = -6D\gamma^3 = -3\omega_a^3 \left(m_a^3/2D\right)^{1/2}$, *etc.* Now, taking the interaction in the lowest (harmonic) approximation, we have $\Pi = -i\lambda_2$, and the Dyson equation $\Gamma_0 = \Gamma_{00} + \Gamma_{00}\,\Pi\,\Gamma_0$ gives the Green function obtained in Sec. 8.14:

$$\Gamma_0(\omega) = \frac{i}{m_a} \, \frac{1 + \frac{m_a}{m_s}\omega^2 \mathcal{D}_s}{\omega^2 - \omega_a^2\left(1 + \frac{m_a}{m_s}\omega^2 \mathcal{D}_s\right) + i\delta}\,. \tag{9.34}$$

decay of local vibration to phonons ...
phonon loop ...
SCF theory ...
decay to e-h pairs ...

Chapter 11

Definitions and Useful Formulas

11.1 Delta- and theta-Functions

Define everywhere:

$$\delta \to 0\,, \quad \delta > 0\,. \tag{11.1}$$

$$\Theta(z) = \begin{cases} 1 & \text{if} \quad z > 0\,, \\ 0 & \text{if} \quad z \leq 0\,. \end{cases} \tag{11.2}$$

$$\delta_k = \begin{cases} +\delta & \text{if} \quad \varepsilon_k > \varepsilon_F\,, \\ -\delta & \text{if} \quad \varepsilon_k < \varepsilon_F\,. \end{cases} \tag{11.3}$$

Thus

$$\frac{1}{\epsilon \pm i\delta} = \frac{1}{\epsilon} \mp i\pi\delta(\epsilon) \tag{11.4}$$

(proof: e.g., see Reims p.298)

$$\frac{d\Theta(z)}{dz} = \delta(z) \tag{11.5}$$

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dx\, e^{-ixt} = \frac{1}{2\pi i}\left(\frac{1}{t - i\delta} - \frac{1}{t + i\delta}\right) \tag{11.6}$$

$$\Theta(z) = \int_{-\infty}^{z} dt\, e^{\delta t}\delta(t) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} dx\, \frac{e^{-ixt}}{x + i\delta} \tag{11.7}$$

$$f(x)\delta(x) = f(0)\delta(x) \tag{11.8}$$

11.2 Many-Particle Problem

$$\eta = \pm 1 \quad \text{for} \quad \begin{Bmatrix} \text{Bose} \\ \text{Fermi} \end{Bmatrix} \quad \text{particles} \tag{11.9}$$

$$[A, B]_\eta = AB - \eta BA\,. \tag{11.10}$$

Define:

Φ_0 is the *exact* normalized wave function of the *ground state* of the system of N *noninteracting fermions*;

Φ_n is the exact normalized wave function of an *excited state* of the system of N noninteracting

fermions;
H_0 is the Hamiltonian of noninteracting fermions,

$$H_0\Phi_0 = E_0\Phi_0\,, \quad H_0\Phi_n = E_n\Phi_n\ ; \tag{11.11}$$

Ψ_0 is the *exact* normalized wave function of the *ground state* of the system of N *interacting fermions*;
$H = H_0 + V$ is the Hamiltonian of interacting fermions,

$$H\Psi_0 = E_0^{\rm exact}\Psi_0, \quad E_0^{\rm exact} = E_0 + \Delta E\ ; \tag{11.12}$$

$\Psi_n^{(N)}$ is the exact normalized wave function of an *excited state* of the system of N interacting fermions,

$$H\Psi_n^{(N)} = E_n^{\rm exact}\Psi_n^{(N)}, \quad \hbar\omega_{n0} = E_n^{\rm exact} - E_0^{\rm exact}, \tag{11.13}$$

$$E_n^{\rm exact} = E_n + \Delta E_n, \tag{11.14}$$

and $E_{\rm corr} = E_0^{\rm exact} - E_0^{\rm HF}$ is called by the *correlation energy.*

The *evolution operator* is defined as

$$U(t - t_0) = U(t, t_0) = e^{-i\frac{H}{\hbar}t}. \tag{11.15}$$

It satisfies the equation

$$i\hbar\frac{\partial U(t,t_0)}{\partial t} = HU(t,t_0)\,, \quad U(0) = 1\,. \tag{11.16}$$

The evolution operator is the unitary operator,

$$U^*(t,t_0) = U^{-1}(t,t_0) = U(t_0,t)\,, \tag{11.17}$$

and also

$$U(t_3,t_2)U(t_2,t_1) = U(t_3,t_1)\,. \tag{11.18}$$

Formal solution of the Schrödinger equation can be written in the following form,

$$|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle\,. \tag{11.19}$$

Define the averaging $\langle\ldots\rangle$ for the $T = 0$ case as

$$\langle\ldots\rangle = \langle\Psi_0|\ldots|\Psi_0\rangle \tag{11.20}$$

(the case of $T > 0$ will be described below).

The *chronological operators* are defined as follows,

$$P_{\rm ch}[A(t_1)\,B(t_2)] = \begin{cases} A(t_1)B(t_2) & \text{if} \quad t_1 > t_2\,, \\ B(t_2)A(t_1) & \text{if} \quad t_1 < t_2\,, \end{cases} \tag{11.21}$$

$$T_{\rm ch}[A(t_1)\,B(t_2)] = \begin{cases} A(t_1)B(t_2) & \text{if} \quad t_1 > t_2\,, \\ \eta B(t_2)A(t_1) & \text{if} \quad t_1 < t_2\,. \end{cases} \tag{11.22}$$

For Fermi operators

$$T_{\rm ch}\{A_1(t_1)\ldots A_n(t_n)\} = (-1)^p A_{\alpha_1}(t_{\alpha_1})\ldots A_{\alpha_n}(t_{\alpha_n})\,, \tag{11.23}$$

where $t_{\alpha_1} > \ldots > t_{\alpha_n}$, and p is the number of permutation made.

Table 11.1: Atomic units

type	$\hbar$	a_{Bohr}	m_{el}	e	unit of energy	kin. energy	pot. en.	c	m_{proton}
I	1	1	1	1	2 Ry = 27.2 eV	$\frac{1}{2}p^2 = -\frac{1}{2}\nabla^2$	$\mp 1/r$	137.2	1836
II	1	1	1/2	$\sqrt{2}$	1 Ry = 13.6 eV	$p^2 = -\nabla^2$	$\mp 2/r$		918

Normal product $\mathcal{N}$: reordering so that all creation operators are at the left of all annihilation operators, multiplied by the factor $(-1)^p$,

$$T_{\text{ch}}(AB) = \mathcal{N}(AB) + \overbrace{AB}\,, \tag{11.24}$$

Equation (11.24) is the definition of $\overbrace{AB}$.

$$T_{\text{ch}}[A(t)\,A^*(t)] = -A^*(t)A(t)\,. \tag{11.25}$$

Also for the electron gas:
r_0 is defined as $V_{\text{volume}} = N\frac{4}{3}\pi r_0^3$,
r_s is defined as $r_s = r_0/a_{\text{Bohr}}$, it is dimensionless, for metals $r_s \sim 2-6$

$$k_F = \frac{1}{0.52 r_0} = \frac{3.64}{r_s}\text{Å}^{-1}, \tag{11.26}$$

$$\varepsilon_F = \frac{3.68}{r_s^2}\ \text{Ry}. \tag{11.27}$$

11.3 Atomic System of Units

There are two popular system of units described in Table 11.1.

11.4 Representations

Heisenberg representation

$$A^{(\text{G})}(t) = e^{\frac{iHt}{\hbar}} A^{(\text{S})} e^{-\frac{iHt}{\hbar}} \tag{11.28}$$

11.5 Statistical Mechanics

Averaging for $T > 0$ (the Great Canonical Ensemble)

$$\langle \ldots \rangle = Q^{-1}\,\text{Sp}\left(e^{-\beta\mathcal{H}}\ldots\right) \tag{11.29}$$

where $\beta = (k_B T)^{-1}$,

$$Q = \text{Sp}\left(e^{-\beta\mathcal{H}}\right) \tag{11.30}$$

$$\mathcal{H} = H - \mu N \tag{11.31}$$

and Sp is the sum over the number of particles in the system, and over all possible states of the system for a given number of particles.

11.6 Solid State

Because many examples are taken from Solid State Theory, let us summarize here its main issues. For more details, see textbooks of Ziman (the best), Kittel (3 books).

11.6.1 Definitions

Let us define:
V is the volume.

Direct lattice:
$\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the primitive vectors,
Wigner-Seitz cell is the elementary cell,
Bravais cell if there is only *one* atom in the elementary cell,
Bravais lattice consists of Bravais cells,
$\mathbf{l} = l_1\mathbf{a_1} + l_2\mathbf{a_2} + l_3\mathbf{a_3}$, where l_i are integers,
$\Omega_0 = \mathbf{a_1} \cdot [\mathbf{a_2} \times \mathbf{a_3}]$ is the cell volume.

Inverse lattice:
$\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are the primitive vectors of the inverse lattice defined by

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\Omega_0}, \quad \mathbf{a_i} \cdot \mathbf{b_k} = 2\pi \delta_{ik}, \tag{11.32}$$

Brillouin zone is the WignerSeitz cell in the inverse lattice,
$\mathbf{g} = g_1\mathbf{b_1} + g_2\mathbf{b_2} + g_3\mathbf{b_3}$, where g_i are integers,
$\Omega_0^* = (2\pi)^3/\Omega_0$,
Miller indexes (h,k,l) of a given plane are the inverse values of the sections cut by the plane from the axes,
if $g_1 : g_2 : g_3 = h : k : l$, then $\mathbf{g}$ is perpendicular to the plane (h,k,l),
the distance between two nearest neighboring planes is

$$d(h,k,l) = \frac{2\pi}{|\mathbf{g}_{hkl}|}. \tag{11.33}$$

Cyclic boundary conditions:
Discrete case:
$q_r = N^{-1/2} \sum_k Q_k \exp(ikra)$, where $r = 1, 2, \ldots, N$,
$Q_r = N^{-1/2} \sum_s q_s \exp(-iksa)$,
cyclic: $q_{r+N} = q_r$, therefore $\exp(ikNa) = 1$, or

$$k = \frac{2\pi}{Na} n, \quad \text{where} \quad n = 0, \pm 1, \ldots, \pm\left(\frac{N}{2} - 1\right), +\frac{N}{2}. \tag{11.34}$$

Continuous case:
$q(x) = L^{-1/2} \sum_k Q_k \exp(ikx)$, where $-\frac{1}{2}L < x < +\frac{1}{2}L$,
$Q_k = L^{-1/2} \int_{-\frac{1}{2}L}^{+\frac{1}{2}L} dx\, q(x) \exp(-ikx)$,
cyclic: $q(x+L) = q(x)$, therefore $\exp(ikL) = 1$, or

$$k = \frac{2\pi}{L} n, \quad \text{where} \quad n = \text{integer}. \tag{11.35}$$

Fourier series:
if $f(\mathbf{x}) = f(\mathbf{x}+\mathbf{l})$, then $f(\mathbf{x}) = \sum_{\mathbf{g}} a_{\mathbf{g}} \exp(i\mathbf{g}\mathbf{x})$, where $a_{\mathbf{g}} = \Omega_0^{-1} \int_{\text{cell}} d\mathbf{x}\, f(\mathbf{x}) \exp(-i\mathbf{g}\mathbf{x})$.
Note: $\int_{\text{cell}} d\mathbf{x}\, f(\mathbf{x}) \exp(i\mathbf{K}\mathbf{x}) = 0$ if $\mathbf{K} \neq \mathbf{g}$.

Approximations: When electronic states are considered, usually one uses
(i) the adiabatic approximation, and
(ii) the one-electron approximation, i.e. $V(r)$ should be self-consistent (although the energies may be calculated rather accurate, wavefunctions cannot, typically).

Schemes:
reduced zones: quantum numbers k and n, where $-\pi < k \le \pi$ and $n = 0, 1, 2, \ldots$
repeated zones: quantum numbers k and n, where $-\infty < k < \infty$ and $n = 0, 1, 2, \ldots$ (this scheme is overcomplete);
extended zones: quantum number k, where $-\infty < k < \infty$.

In the scheme of reduced zones the number of k values in the Brillouin zone is equal to the number of elementary cells in the unit of volume in the direct lattice,

$$\sum_{k,\sigma} \ldots \to 2(\text{spin}) \frac{V}{(2\pi)^3} \int d^3k \ldots = 2(\text{spin}) \frac{N}{\Omega_0^*} \int d^3k \ldots \tag{11.36}$$

Useful formulas:

$$\int_V d\mathbf{x}\, e^{i\mathbf{k}\mathbf{x}} = V \delta_{\mathbf{k},0} \tag{11.37}$$

$$\sum_{\mathbf{l}} e^{-i\mathbf{k}\mathbf{l}} = N\delta_{\mathbf{k},\mathbf{g}}, \quad \sum_{\mathbf{k}} e^{+i\mathbf{k}\mathbf{l}} = N\delta_{\mathbf{l},0} \tag{11.38}$$

$$\frac{1}{|\mathbf{r}|} = \frac{4\pi}{V} \sum_{\mathbf{q}} \frac{1}{q^2} e^{+i\mathbf{q}\mathbf{r}}. \tag{11.39}$$

Ewald method of calculation of a lattice sum:

$$\sum_{\mathbf{l}} \frac{e^{i\mathbf{q}\mathbf{l}}}{|\mathbf{l}-\mathbf{r}|} = \underbrace{\sum_{\mathbf{l}} \frac{e^{i\mathbf{q}\mathbf{l}}}{|\mathbf{l}-\mathbf{r}|} \operatorname{erfc}(a|\mathbf{l}-\mathbf{r}|)}_{\text{direct lattice}} + \frac{\pi}{\Omega_0} \frac{1}{a^2} \underbrace{\sum_{\mathbf{g}} \frac{e^{i(\mathbf{q}+\mathbf{g})\cdot\mathbf{r}} e^{-|\mathbf{q}+\mathbf{g}|^2/4a^2}}{|\mathbf{q}+\mathbf{g}|^2/4a^2}}_{\text{inverse lattice}}, \tag{11.40}$$

where a is arbitrary and $\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty du\, e^{-u^2}$.

11.6.2 Density of states

The density of states $\mathcal{N}(\varepsilon)$ is defined so that $\mathcal{N}(\varepsilon)\, d\varepsilon$ is equal to the number of states with energies between ε and $\varepsilon + d\varepsilon$ per unit volume of the crystal (the sum over spin is omitted),

$$\mathcal{N}(\varepsilon_0) = \frac{d}{d\varepsilon_0} \frac{1}{(2\pi)^3} \iiint_{\varepsilon(\mathbf{k})<\varepsilon_0} d^3k = \frac{1}{(2\pi)^3} \iint_{\varepsilon(\mathbf{k})=\varepsilon_0} \frac{dS}{|\nabla\varepsilon(\mathbf{k})|}. \tag{11.41}$$

The function $\mathcal{N}(\varepsilon)$ is continuous, but it derivative has peculiarities at the points where $\nabla\varepsilon(\mathbf{k}) = 0$. Near such a point k_0 the energy may be expanded as

$$\varepsilon(\mathbf{k}) = \varepsilon(\mathbf{k}_0) + \alpha_1(k_1 - k_{01})^2 + \alpha_2(k_2 - k_{02})^2 + \alpha_3(k_3 - k_{03})^2 + \ldots, \tag{11.42}$$

where k_1, k_2 and k_3 are the principal axes. The function $\mathcal{N}(\varepsilon)$ may have the following peculiarities:

(1) *maximum*, when $\alpha_1 < 0$, $\alpha_2 < 0$ and $\alpha_3 < 0$. From the analytical geometry (volume of ellipsoidal) it follows that a neighboring of the point $\mathbf{k}_0$ gives the contribution into the density of states, equal to

$$\Delta\mathcal{N}(\varepsilon) = \frac{1}{4\pi^2}\frac{\Theta\left(\varepsilon(\mathbf{k}_0) - \varepsilon\right)}{\sqrt{|\alpha_1\alpha_2\alpha_3|}}\sqrt{\varepsilon(\mathbf{k}_0) - \varepsilon} \tag{11.43}$$

(2) *minimum* (a local minimum as well), $\alpha_1 > 0$, $\alpha_2 > 0$ and $\alpha_3 > 0$, gives the contribution

$$\Delta\mathcal{N}(\varepsilon) \propto \sqrt{\varepsilon - \varepsilon(\mathbf{k}_0)} \tag{11.44}$$

(3) *saddle* type s$_1$, $\alpha_1 > 0$, $\alpha_2 < 0$ and $\alpha_3 < 0$, gives the contribution

$$\Delta\mathcal{N}(\varepsilon) \propto -\sqrt{\varepsilon - \varepsilon(\mathbf{k}_0)} \tag{11.45}$$

(4) *saddle* type s$_2$, $\alpha_1 > 0$, $\alpha_2 > 0$ and $\alpha_3 < 0$, gives the contribution

$$\Delta\mathcal{N}(\varepsilon) \propto -\sqrt{\varepsilon(\mathbf{k}_0) - \varepsilon}. \tag{11.46}$$

van-Hove theorem:
(1) any spectrum must have at least one s$_1$-type peculiarity and at least one s$_2$-type peculiarity,
(2) at the top boundary of the spectrum we always have $d\mathcal{N}(\varepsilon)/d\varepsilon = -\infty$.

Besides, $\mathcal{N}(\varepsilon)$ has also a cusp peculiarity when a surface of constant energy touches the Brillouin zone.

11.6.3 Electrodynamics

Maxwell equations

Denote by:
q is the charge (1 C $= 3 \cdot 10^9$ CGSE),
φ is the potential (1 V $= \frac{1}{300}$ CGSE),
p is the dipole (1 C·m $= 3 \cdot 10^{11}$ CGSE);
ρ_{ext} and j_{ext} are the density of external charge and current respectively (1 A/m^2 $= 3 \cdot 10^5$ CGSE);
E is the macroscopic (averaged over the elementary cell) electric field (1 V/m $= \frac{1}{3} \cdot 10^{-4}$ CGSE);
P is the polarization (dipole momentum of a volume unit) (1 C/m^2 $= 3 \cdot 10^5$ CGSE);
D is the electrical induction (displacement) (C/m^2);
H is the macroscopic (averaged over the elementary cell) magnetic field (1 A/m $= 4\pi \cdot 10^{-3}$ Ersted);
M is the magnetization (magnetic momentum of a volume unit);
B is the magnetic induction (1 Tesla $= 10^4$ Gauss);
ϵ is the dielectric permittivity, and σ is the conductivity (conditional division on displacement current and real current);
μ is the magnetic permeability;
$\chi_{\text{el, mag}}$ is the susceptibility.

The Maxwell equations in a solid state have the following form:

CGSE	SI
$D = E + 4\pi P$ $= \epsilon E$ $= (1 + 4\pi\chi_{\mathrm{el}})E$ where $P = \chi_{\mathrm{el}} E$ (definitions)	$D = \epsilon_0 E + P$ $= \epsilon_0(1 + \chi_{\mathrm{el}})E$ $= \epsilon_0 \epsilon E$
$\nabla \cdot D = 4\pi\rho_{\mathrm{ext}}$ (follows from $\nabla \cdot P = -\rho_{\mathrm{polarization}}$)	$\nabla \cdot D = \rho_{\mathrm{ext}}$
$\nabla \times E = -\frac{1}{c}\frac{\partial B}{\partial t}$ (the same as in vacuum)	$\nabla \times E = -\frac{\partial B}{\partial t}$
$B = H + 4\pi M$ $= \mu H$ $= (1 + 4\pi\chi_{\mathrm{mag}})H$ where $M = \chi_{\mathrm{mag}} H$ (definitions)	$B = \mu_0(H + M)$ $= \mu_0(1 + \chi_{\mathrm{mag}})H$ $= \mu\mu_0 H$
$\nabla \cdot B = 0$ (the same as in vacuum)	$\nabla \cdot B = 0$
$\nabla \times H = \frac{4\pi}{c} j_{\mathrm{ext}} + \frac{1}{c}\frac{\partial D}{\partial t}$ where $j_{\mathrm{ext}} = \sigma E$ (follows from $j_{\mathrm{polarization}} = \frac{\partial P}{\partial t}$)	$\nabla \times H = j_{\mathrm{ext}} + \frac{\partial D}{\partial t}$
density of energy $= \frac{1}{8\pi}\left(\epsilon E^2 + \mu H^2\right)$ $= \frac{1}{8\pi}\left(E \cdot D + H \cdot B\right)$	density of energy $= \frac{1}{2}\left(\epsilon_0 \epsilon E^2 + \mu_0 \mu H^2\right)$
vacuum: $\epsilon = 1$ $\sigma = 0$ $\mu = 1$ $\chi_{\mathrm{el}} = \chi_{\mathrm{mag}} = 0$	vacuum: $\epsilon_0 = \frac{10^7}{4\pi c^2} = \frac{1}{4\pi \cdot 9 \cdot 10^9}$ F/m $\mu_0 = 4\pi \cdot 10^{-7}$ Henry/m

Boundary condition: D and B must be continuous at the boundaries.

The permeability introduced above is not a scalar but a tensor. For example, the electrical one is defined as (Landau X part III):

$$E_i = \left[\epsilon^{-1}\right]_{ik} D_k. \tag{11.47}$$

If a solid is (i) homogeneous, (ii) isotropic, and (iii) optically inactive (?), then the permeability may be presented as

$$\epsilon_{ik}(q\omega) = \epsilon_l(q\omega)\frac{q_i q_k}{q^2} + \epsilon_t(q\omega)\left(\delta_{ik} - \frac{q_i q_k}{q^2}\right). \tag{11.48}$$

Here:
$\epsilon_l(q\omega)$ is the *longitudinal permeability*, it describes a response to an external charge, i.e. if the

field is potential, $E = -\nabla\varphi$, then $\mathbf{D} = \epsilon_l \mathbf{E}$, and
$\epsilon_t(q\omega)$ is the *transverse permeability*, it describes a response to an external electromagnetic field, i.e. if the field is solenoidal, $\nabla \cdot E = 0$, then $\mathbf{D} = \epsilon_t \mathbf{E}$.
Both these functions are generalized susceptibilities (but different!) and are described in Sec. 8.14.

Metals

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Semiconductors

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Dielectrics

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