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Chapter 13

Introductory Many-Body Physics

> *Muchos pocos hacen un mucho.*
> *(Many a pickle makes a mickle [30])*
> — *Miguel de Cervantes, Don Quixote.*

13.1 Introduction

In the last chapter, the quantum nature of a system of identical particles was introduced. A number of importance consequences, such as the construction of the periodic table of elements and the shell theory of nuclei, were deduced based on the independent-particle model, in which the interaction between particles was represented by part of the one-particle potential without specifying how it was to be approximated. In this chapter, we introduce the construction of one-particle potentials whose purpose is to take into account the many-body effects on the single-particle dynamics, in particular, the Hartree and Fock approximations and the density functional theory. The last is the framework for the Thomas-Fermi approximation and its systematic density-gradient corrections. It is also the basis for the local-density approximation, which has been widely used, especially by solid state physicists and quantum chemists. By a slight extension of the Hartree-Fock methodology, we study the theory of fermion pairing in the Bardeen-Cooper-Schrieffer (BCS) state, which has applications in superconductors, the physics of the nucleus, and particle theory.

The method of second quantization will be first introduced as a concise way to deal with many-body systems and as a convenient conceptual tool to understand the physics. Thus, I hope that this chapter would also serve as a preliminary step to further study in quantum field theory and in many-body physics.

13.2 Second Quantization

In principle, we can gain complete knowledge of a many-particle systems by writing down the Hamiltonian for this system and solve the Schrödinger equation associated with it. However, the Hamiltonian typically contains, besides the sums of single-particle kinetic energy and static potential, the interaction between pairs of particles. This makes the partial differential equation of many-particle coordinates not separable. The resource required for direct numerical solution beyond a few particles is prohibitive.

One might imagine that one could start with a complete set of one-particle states and construct all the symmetrized (for bosons) and antisymmetrized (for fermions) states as the basis set for the N-particle state. The problem is then reduced to diagonalizing a matrix of the Hamiltonian. Of course, the size of the matrix grows exponentially with N. Nonetheless the idea of independent-particle basis states is a useful one as a starting point for building approximations. One needs a better tool than working directly with the sum of symmetrized products (permanents) or Slater determinants introduced in the last chapter. Second quantization is the tool which facilitates the construction of a complete set of basis sets for any number of particles. The idea is to use an operator to connect one state of a definite number of particles to a state with one more or less particle. The operator also contains the dynamical information of the particle added or removed. The most general state can then be expressed as a linear combination of these basis states.

13.2.1 The creation operator

In the beginning, there is void. We describe the state with no particles as the vacuum, denoted by $|0\rangle$, the first state vector in the Hilbert space. Then, we put one particle at the position r, given by the state vector

$$|r\rangle = \psi^\dagger(r)|0\rangle, \tag{13.2.1}$$

where we have introduced the creation operator $\psi^\dagger(r)$ describing the act of creating a particle at r out of the void. For definiteness, we will focus our attention on r as the position coordinates of a particle. If we wish to include additional independent degrees of freedom for a particle such as spin, we could include in r the eigenvalues of S^2 and $\mathbf{S}\cdot\hat{n}$, etc. Since identical particles have the same fixed spin s, we need only include the azimuthal quantum number m_s along a specified direction z. In principle, the spins of the particles can have different orientations $\hat{n}$ but an equivalent description is to use the same basis set of eigenstates along a common fixed z direction and to specify the spin components for various m_s. Similarly, we could add an isospin quantum number of T_3 for a nucleon. In general, r represents a set of quantum numbers which yield a complete set of one-particle states, such as $n\ell m m_s$ for an electron in an atom.

One function of the creation operator $\psi^\dagger(r)$ is to transform the vacuum state to the one-particle state $|r\rangle$. The idea of the creation operator is not totally new to us. We have encountered a couple of examples before. The creation operation in the harmonic oscillator problem which gives $c^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ connects a state with n quanta of energy $\hbar\omega$ (plus the zero point energy $\hbar\omega/2$) to the state with $n+1$ quanta of energy. The raising operator L_+ connects the angular momentum state $|\ell\, m\rangle$ to $|\ell\, m+1\rangle$. The only difference is that the one-particle state has to be characterized, in addition, by the quantum numbers for a complete set of one-particle basis states, such as r.

Now, for a state with the first particle at r_1 and the second particle at r_2, we could use the description

$$|r_2, r_1\rangle = |r_2\rangle_2 |r_1\rangle_1, \tag{13.2.2}$$

where the right-hand side describes the Hilbert space made up of a product of two single-particle particle Hilbert spaces, with the particle at r_1 in one and the particle at r_2 in the second. (Notice that we arrange the order of the Hilbert spaces of the individual particles from right to left, opposite to the convention commonly used, cf. Sec. 11.3). Its relation to the vacuum is

$$|r_2, r_1\rangle = \psi^\dagger(r_2)\phi^\dagger(r_1)|0\rangle. \tag{13.2.3}$$

This recipe is OK if the two particles are distinct, such as a proton and an electron, represented by two different creation operators which commute with each other. If the two particles are identical, we need (1) the two operators to be identical except for the dependence on the quantum number, r_1 or r_2 and (2) their algebra reflects the permutation symmetry of the boson or fermion character.

For bosons, the two-particle state has to be symmetrized:

$$S|r_2, r_1\rangle = \frac{1}{\sqrt{2}}[|r_2\rangle_2|r_1\rangle_1 + |r_1\rangle_2|r_2\rangle_1]. \tag{13.2.4}$$

The normalization factor of $1/\sqrt{2}$ is determined by the requirement

$$\langle r'1, r_2'|S^\dagger S|r_2, r_1\rangle = \delta(r_2' - r_2)\delta(r_1' - r_1) + \delta(r_2' - r_1)\delta(r_1' - r_2), \tag{13.2.5}$$

where the Hermitian conjugate of the state vector of $|r_2, r_1\rangle$ has the particle positions in reversed order. The state is normalized in the continuous eigenvalue case if one pair of quantum number equal to the other or its exchange. The second act of creation is given by:

$$S|r_2, r_1\rangle = \psi^\dagger(r_2)|r_1\rangle = \psi^\dagger(r_2)\psi^\dagger(r_1)|0\rangle. \tag{13.2.6}$$

The symmetry of the state under particle exchange demands the commutation relation,

$$\psi^\dagger(r_2)\psi^\dagger(r_1) = \psi^\dagger(r_1)\psi^\dagger(r_2), \tag{13.2.7}$$

or

$$[\psi^\dagger(r_1), \psi^\dagger(r_2)] \equiv \psi^\dagger(r_1)\psi^\dagger(r_2) - \psi^\dagger(r_2)\psi^\dagger(r_1) = 0. \tag{13.2.8}$$

If the particles are fermions, the two-particle state has to be antisymmetrized:

$$A|r_2, r_1\rangle = \frac{1}{\sqrt{2}}\left[|r_2\rangle_2|r_1\rangle_1 - |r_1\rangle_2|r_2\rangle_1\right]. \tag{13.2.9}$$

In second quantized form, the state is given by

$$A|r_2, r_1\rangle = \psi^\dagger(r_2)\psi^\dagger(r_1)|0\rangle. \tag{13.2.10}$$

The antisymmetry of the state under particle exchange demands the anticommutation relation,

$$\psi^\dagger(r_2)\psi^\dagger(r_1) = -\psi^\dagger(r_1)\psi^\dagger(r_2), \tag{13.2.11}$$

or

$$\{\psi^\dagger(r_1), \psi^\dagger(r_2)\} \equiv \psi^\dagger(r_1)\psi^\dagger(r_2) + \psi^\dagger(r_2)\psi^\dagger(r_1) = 0. \tag{13.2.12}$$

By induction, the same creation operator can be used to build an N-particle basis state,

$$X_N|r_N, \ldots, r_2, r_1\rangle = \frac{1}{\sqrt{N!}} \sum_P e_P P |r_N\rangle_N \ldots |r_2\rangle_2 |r_1\rangle_1, \tag{13.2.13}$$

where P is the permutation operator acting on permuting the one-particle states among the individual Hilbert spaces. For the bosons, X_N is the symmetrization operator S_N with $e_P = 1$. For the fermions, X_N is the antisymmetrization operator A_N with $e_P = \pm 1$ depending on the parity of the permutation (i.e. on whether the number of exchanges is even or odd). To add a particle to an N-particle state, the rule is

$$\psi^\dagger(r_{N+1}) X_N |r_N, \ldots, r_2, r_1\rangle = X_{N+1}|r_{N+1}, r_N, \ldots, r_2, r_1\rangle \tag{13.2.14}$$

For each N-particle space, we have a complete set of position eigenstates

$$X_N|r_N, \ldots, r_2, r_1\rangle = \psi^\dagger(r_N)\psi^\dagger(r_{N-1}) \ldots \psi^\dagger(r_1)|0\rangle, \tag{13.2.15}$$

whose boson or fermion property simply depends on the commutation rule. In the representation of the symmetrized state in the second quantized form, the order of labeling the individual particle Hilbert spaces is no longer important.

13.2.2 The annihilation operator

In this subsection, we show that $\psi(r)$, the Hermitian conjugate of the creation operator $\psi^\dagger(r)$, removes a particle at r if there is one there and destroys the whole state if there is no particle at r.

The Hermitian conjugate of the state $\psi^\dagger(r)|0\rangle$ is $\langle 0|\psi(r)$. The overlap of two states is given by

$$\langle r'|r\rangle = \langle 0|\psi(r')\psi^\dagger(r)|0\rangle. \tag{13.2.16}$$

We may read the above equation as showing that the action of $\psi(r')$ following the creation of a particle is to reduce the one-particle state to a zero-particle state. Because of the orthonormality of the position eigenstates, given by

$$\langle r'|r\rangle = \delta(r - r'), \tag{13.2.17}$$

the annihilation operator $\psi(r')$ reduce the one-particle state to vacuum if it hits exactly where the existing particle is but destroys the vacuum state on the right if it does not hit the particle. Thus, two important properties of the annihilation operator ensue. One is the reduction of the vacuum state to nothingness,

$$\psi(r)|0\rangle = 0. \tag{13.2.18}$$

The use of the words, “void” and “nothingness” seems Zen-like but the distinction is perfectly precise. The void or the vacuum state is a state of the Hilbert space with no particles (or at least no particles of the kind under consideration) whereas nothingness means no state in the Hilbert space at all. The second property is the commutation relations, which for the bosons and fermions are, respectively,

$$[\psi(r), \psi^\dagger(r')] = \delta(r - r'), \tag{13.2.19}$$

$$\{\psi(r), \psi^\dagger(r')\} = \delta(r - r'). \tag{13.2.20}$$

Note that if r contains a component of discrete quantum numbers, such as the spin, $r = (\mathbf{r}.m_s)$, then

$$\delta(r - r') = \delta(\mathbf{r} - \mathbf{r}')\delta_{m_s,m_s'}. \tag{13.2.21}$$

The commutation relations between $\psi^\dagger(r)$ and $\psi^\dagger(r')$ lead to their Hermitian conjugate relations, for bosons and fermions respectively,

$$[\psi(r), \psi(r')] = 0, \tag{13.2.22}$$

$$\{\psi(r), \psi^\dagger(r')\} = 0. \tag{13.2.23}$$

In general, the destruction effect is

$$\psi(r)X_N|r_N, \ldots, r_1\rangle = \sum_{\ell=1}^{N} e_\ell \delta(r - r_\ell) X_{N-1}|r_N, \ldots, (r_\ell \text{ removed}), \ldots, r_1\rangle, \tag{13.2.24}$$

where e_ℓ is unity for the bosons and is the parity symbol for the fermions. The parity $e_\ell = \pm 1$ depends on the even or odd number of exchanges necessary for the annihilation operator $\psi(r)$

to get to $\psi^\dagger(r_\ell)$, It follows that

$$\begin{aligned}\langle 0|\psi(r_1')\ldots,\psi(r_N')\psi^\dagger(r_N)\ldots\psi^\dagger(r_1)|0\rangle &= \sum_P e_P P\{r_j\}\prod_{j=1}^N \langle 0|\psi(r_j')\psi^\dagger(r_j)|0\rangle \\ &= \sum_P e_P P\{r_j\}\prod_{j=1}^N \delta(r_j'-r_j), \qquad (13.2.25)\end{aligned}$$

where $P\{r_j\}$ denotes a permutation of the variables $r_1, r_2, \ldots, r_N$. This useful result of breaking an expectation value of an "anti-normal" product of annihilation and creation operators (i.e., annihilation operators to the left of the creation operators) into a sum of permutation of expectation values of pairs of an annihilation and a creation operator, $\langle r_{j'}'|r_j\rangle$, is a special case of the Wick's theorem. It can be proved either from the definition of the symmetrized (or antisymmetrized) state, $\langle r_1', \ldots, r_N'|X_N^\dagger X_N|r_N, \ldots, r_1\rangle$, or directly from the commutation of the operators, such as Eq. (13.2.24).

Working in terms of the representation of a complete basis set, we often make use of the completeness relation. Here it is, in terms of the unsymmetrized states,

$$\int dr_N \ldots \int dr_1 |r_N \ldots r_1\rangle\langle r_1 \ldots r_N| = 1. \qquad (13.2.26)$$

Since this operators between two states which are always either symmetric or antisymmetric, we can replace the left-hand side by the symmetrized version,

$$\int dr_N \ldots \int dr_1 X_N |r_N \ldots r_1\rangle \frac{1}{N!}\langle r_1 \ldots r_N| X_N = 1, \qquad (13.2.27)$$

or, in the second quantized form,

$$\int dr_N \ldots \int dr_1 \psi^\dagger(r_N)\psi^\dagger(r_{N-1})\ldots\psi^\dagger(r_1)|0\rangle \frac{1}{N!}\langle 0|\psi(r_1)\ldots\psi(r_N) = 1, \qquad (13.2.28)$$

When each state in the completeness relation is replaced by a sum of $N!$ permuted terms, the whole integral needs to be divided by $N! \times N!$ terms. The absorption of $\sqrt{N!}$ in each X_N leaves only $N!$ in the denominator.

13.2.3 Second quantization of the physical observable

If the mapping of the momentum $\mathbf{p}$ to the operator $-i\hbar\nabla$ is regarded as the first quantization, then the change of the wave function to the operator $\psi(r)$ may be considered as the second quantization. The wave function of an N-particle state represented by a symmetric or antisymmetric state vector $|\Psi\rangle$ is given by

$$\begin{aligned}\langle r_N, r_{N-1}, \ldots, r_1|\Psi\rangle &= \frac{1}{\sqrt{N!}}\langle r_N, r_{N-1}, \ldots, r_1|X_N|\Psi\rangle \\ &= \frac{1}{\sqrt{N!}}\langle 0|\psi(r_N)\ldots\psi(r_1)|\Psi\rangle. \qquad (13.2.29)\end{aligned}$$

Note that the bra state on the left is not symmetrized. One advantage which we shall demonstrate presently is the convenience of second quantization for dealing with many-particle states. An important concept is that we have transformed the treatment of the many-particle system into a treatment of the particle field $\psi(r)$. We shall later see that the quantization of the electromagnetic field is closely related to the particle field.

We need a way to represent the physical observable in the first quantization in terms of the creation and annihilation operators.

The density and number operators

First consider the Hermitian operator

$$\hat{n}(r) = \psi^\dagger(r)\psi(r). \qquad (13.2.30)$$

Since

$$\hat{n}(r)\psi^\dagger(r_1)\ldots\psi^\dagger(r_N)|0\rangle = \sum_{j=1}^{N}\delta(r-r_j)\psi^\dagger(r_1)\ldots\psi^\dagger(r_N)|0\rangle, \qquad (13.2.31)$$

using the commutation or anticommutation relations and since the sum of the δ-functions gives the density of particles in the system, we can interpret the operator $\hat{n}(r)$ as the number density operator. Similarly,

$$\hat{N} = \int dr\, \hat{n}(r) = \int dr\, \psi^\dagger(r)\psi(r), \qquad (13.2.32)$$

is the total number operator, since

$$\hat{N}\psi^\dagger(r_1)\ldots\psi^\dagger(r_N)|0\rangle = N\psi^\dagger(r_1)\ldots\psi^\dagger(r_N)|0\rangle. \qquad (13.2.33)$$

One-particle properties

A one-particle observable is a function of position, momentum, spin, etc., of a particle, $f(r,p)$, where p includes the dynamic operators in the $|r\rangle$ representation not in the set of operators producing the eigenvalues r, such as the momentum operator and spin components S_x and S_y. For the N-particle system, the sum of the identical property over all particles is given by the observable

$$F(r_1,p_1,\ldots,r_N,p_N)=\sum_{j=1}^{N}f(r_j,p_j). \tag{13.2.34}$$

Its matrix element between any two N-particle states is given by

$$\langle\Phi|F|\Psi\rangle=\int dr_1\ldots\int dr_N\langle\Phi|r_1\ldots r_N\rangle\sum_{j=1}^{N}f(r_j,p_j)\langle r_N\ldots r_1|\Psi\rangle \tag{13.2.35}$$

$$= N\int dr_1\ldots\int dr_N\langle\Phi|r_1\ldots r_N\rangle f(r_1,p_1)\langle r_N\ldots r_1|\Psi\rangle$$

$$= \frac{1}{(N-1)!}\int dr_1\ldots\int dr_N\langle\Phi|\psi^\dagger(r_1)\ldots\psi^\dagger(r_N)|0\rangle f(r_1,p_1)\langle 0|\psi(r_N)\ldots\psi(r_1)|\Psi\rangle.$$

The first-quantized operator $f(r_1,p_1)$ may be moved to the place just the left of $\psi(r_1)$ since p_1 commutes with all r_j except r_1. The middle two vacuum states may be replaced by a complete set of states of any number of particles without changing the equation since the additional states are orthogonal to the state to the right of $\langle 0|$ or to the left of $|0\rangle$ which has no particles. Thus,

$$\langle\Phi|F|\Psi\rangle$$

$$= \frac{1}{(N-1)!}\int dr_1\ldots\int dr_N\langle\Phi|\psi^\dagger(r_1)\ldots\psi^\dagger(r_N)\psi(r_N)\ldots\psi(r_2)f(r_1,p_1)\psi(r_1)|\Psi\rangle$$

$$= \langle\Phi|\int dr_1\psi^\dagger(r_1)f(r_1,p_1)\psi(r_1)|\Psi\rangle. \tag{13.2.36}$$

Since by Eq. (13.2.33) $\int dr_N\psi^\dagger(r_N)\psi(r_N)=\hat{N}$, operating on the state to the left containing net one-particle, yields a factor of unity, the next integral operates on a two-particle state and so on, successive integration over $r_N, r_{N-1},\ldots,r_2$ gives a factor of $1,2,\ldots,N-1$ which cancels the factorial in the denominator. Hence, the second quantized form of the observable F is

$$\hat{F} = \int dr\, \psi^\dagger(r) f(r,p) \psi(r). \tag{13.2.37}$$

Two important applications of the formula are for the total kinetic energy and potential energy of the system,

$$\begin{aligned}\hat{T} &= \int dr\, \psi^\dagger(r) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi(r) \\ \hat{V} &= \int dr\, \psi^\dagger(r) v(r) \psi(r).\end{aligned} \tag{13.2.38}$$

Two-particle property

We can similarly derive from

$$\langle \Phi | U | \Psi \rangle = \int dr_1 \ldots \int dr_N \langle \Phi | r_1, \ldots, r_N \rangle \, \frac{1}{2} \sum_{j \neq k} u(r_j, p_j; r_k, p_k) \, \langle r_N, \ldots, r_1 | \Psi \rangle, \tag{13.2.39}$$

the second quantized form

$$\hat{U} = \frac{1}{2} \int dr \int dr' \psi^\dagger(r) \psi^\dagger(r') u(r,r') \psi(r') \psi(r) \tag{13.2.40}$$

This is particularly important for the Coulomb interaction between two electrons where

$$u(\mathbf{r} - \mathbf{r}') = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}. \tag{13.2.41}$$

13.2.4 Transformation of the second quantization

We study the transformation from the creation operator $\psi^\dagger(r)$ and annihilation operator $\psi(r)$ in terms of r to another set of quantum numbers. Suppose that a new complete orthonormal set of one-particle states $|u_k\rangle$, $k = 0, 1, \ldots$, is used instead of $|r\rangle$. We choose here to assume the quantum numbers k to be discrete. We can make a series expansion of the annihilation operator as

$$\psi(r) = \sum_k u_k(r) c_k, \tag{13.2.42}$$

where $u_k(r) = \langle r|u_k\rangle$ and

$$c_k = \int dr u_k^*(r)\psi(r), \tag{13.2.43}$$

which may easily be interpreted as an operator which annihilates a particle in state $|u_k\rangle$, just as $c_k^\dagger$ creates a particle in the state

$$|u_k\rangle = c_k^\dagger|0\rangle \tag{13.2.44}$$

since

$$\langle r|c_k^\dagger|0\rangle = \langle 0|\psi(r)\int dr' u_k(r)\psi^\dagger(r)|0\rangle = \langle 0|\int dr'\delta(r-r')u_k(r)|0\rangle = u_k(r). \tag{13.2.45}$$

For the boson operators, the commutation relations are

$$\begin{aligned} [c_k, c_{k'}] &\equiv c_k c_{k'} - c_{k'} c_k = 0; && (13.2.46)\\ \left[c_k, c_{k'}^\dagger\right] &\equiv c_k c_{k'}^\dagger - c_{k'}^\dagger c_k = \delta_{k,k'}. && (13.2.47)\end{aligned}$$

A normalized and symmetrized state made up of N noninteracting bosons is given by

$$\begin{aligned} |j_N, \ldots, j_1\rangle_S &= C(\{j\})S_N[|j_N\rangle_N, \ldots, |j_1\rangle_1]\\ &= C(\{j\})\frac{1}{\sqrt{N!}}\sum_P P[|j_N\rangle_N, \ldots, |j_1\rangle_1], && (13.2.48)\end{aligned}$$

where $C(\{j\})$ is the normalization constant

$$C(\{j\}) = \frac{1}{\sqrt{\prod_k n_k!}}, \tag{13.2.49}$$

to be derived now. Since for bosons, some of the quantum numbers $j_1, \ldots, j_N$ can be the same, let n_k be the number of particles in state k. The number of distinct states after permutation is $N!/\prod_k n_k!$. The normalization constant using the sum of distinct states would be $\sqrt{\prod_k n_k!/N!}$. In using the sum over all permutations we have overcounted the states which should then be divided by $\prod_k n_k!$. Thus,

$$C(\{j\})\frac{1}{\sqrt{N!}} = \sqrt{\frac{\prod_k n_k!}{N!}}\frac{1}{\prod_k n_k!}. \tag{13.2.50}$$

The argument for the normalization constant is illustrated by the consideration of two-boson states in Problem 1. By the definition of the second quantized form in Eq. (13.2.15),

$$c_N^\dagger c_{N-1}^\dagger \dots c_1^\dagger |0\rangle = S_N[|j_N\rangle_N, \dots, |j_1\rangle_1]. \tag{13.2.51}$$

The normalized N-boson state is, therefore,

$$\begin{aligned} |j_N, \dots, j_1\rangle_S &= \frac{1}{\sqrt{\prod_k n_k!}} c_{j_N}^\dagger \dots c_{j_1}^\dagger |0\rangle, & (13.2.52)\\ &= \prod_k \left[\frac{1}{\sqrt{n_k!}} (c_k^\dagger)^{n_k} \right] |0\rangle. & (13.2.53) \end{aligned}$$

For the fermion operators, the commutation relations are

$$\{c_k, c_{k'}\} \equiv c_k c_{k'} + c_{k'} c_k = 0; \tag{13.2.54}$$

$$\{c_k, c_{k'}^\dagger\} \equiv c_k c_{k'}^\dagger + c_{k'}^\dagger c_k = \delta_{k,k'}. \tag{13.2.55}$$

The normalization of the N-fermion state is much simpler since the occupied states $j_1, \dots, j_N$ have to be different from one another:

$$\begin{aligned} |j_N, \dots, j_1\rangle_A &= A_N[|j_N\rangle_N, \dots, |j_1\rangle_1] \\ &= \frac{1}{\sqrt{N!}} \sum_P e_P P[|j_N\rangle_N, \dots, |j_1\rangle_1] \\ &= c_N^\dagger c_{N-1}^\dagger \dots c_1^\dagger |0\rangle. & (13.2.56) \end{aligned}$$

It is, of course, possible to introduce the creation and annihilation operators in terms of the single-particle states and derive the field operator $\psi(r)$ as an expansion in terms of them.

13.3 The Non-interacting Homogeneous Bose Gas

As an example of the use of the second quantization, we study a few key properties of the ideal Bose gas, i.e., a system of N spinless Bose particles which do not interact with each other nor experience an external potential. The Fermi gas is given in Problem 11.

13.3.1 Energy eigenstates

The Hamiltonian is given by

$$H = \sum_j \frac{p_j^2}{2m}. \tag{13.3.1}$$

In second quantized form, it becomes

$$H = \int d^3r \psi^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 \right) \psi(\mathbf{r}). \tag{13.3.2}$$

Since the system is homogeneous, the eigenstate of each particle is a plane-wave state and in that basis, the annihilation operator is written as

$$\psi(\mathbf{r}) = V^{-1/2} \sum_{\mathbf{k}} e^{i\vec{k}\cdot\vec{r}} c_{\mathbf{k}}, \tag{13.3.3}$$

where we have put the bosons in a large box of volume V with periodic boundary conditions. The Hamiltonian becomes

$$H = \sum_{\mathbf{k}} \epsilon_k c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \quad \text{where } \epsilon_k = \frac{\hbar^2 k^2}{2m}. \tag{13.3.4}$$

An energy eigenstate is of the form

$$|\Psi\rangle \equiv |\{n_{\mathbf{k}}\}\rangle = \prod_k \frac{1}{\sqrt{n_{\mathbf{k}}!}} (c_{\mathbf{k}}^\dagger)^{n_{\mathbf{k}}} |0\rangle, \tag{13.3.5}$$

where $\{n_{\mathbf{k}}\}$ denotes a set of occupation functions of single-particle states $\mathbf{k}$. This many-boson state $|\Psi\rangle$ is also an eigenstate of the number operator $c_{\mathbf{k}}^\dagger c_{\mathbf{k}}$ for state $\mathbf{k}$ with the eigenvalue $n_{\mathbf{k}}$.

13.3.2 The pair distribution function

The pair distribution function, $g(\mathbf{r}, \mathbf{r}')$, is the probability of finding a particle at the position $\mathbf{r}$ relative to the position of a particle already known to be at a position $\mathbf{r}'$. By the classical analogy, it may be written as the density-density correlation function,

$$\begin{aligned} g(\mathbf{r}, \mathbf{r}') &= \frac{1}{n^2} \langle \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') \rangle \\ &= \frac{1}{n^2} [\langle \Psi | \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) \psi^\dagger(\mathbf{r}') \psi(\mathbf{r}') | \Psi \rangle], \end{aligned} \tag{13.3.6}$$

where $n = N/V$ is the average density and the angular brackets denotes the expectation value with respect to a state. For convenience of evaluation, the expression is rearranged into the normal order, i.e., the creations operators to the left and the annihilation operators to the right,

$$g(\mathbf{r},\mathbf{r}') = \frac{1}{n^2}[\langle\psi^\dagger(\mathbf{r})\psi(\mathbf{r})\rangle\delta(\mathbf{r}-\mathbf{r}') + \langle\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})\rangle]. \tag{13.3.7}$$

This result is valid for both fermions and bosons. Removing the spiky term, we obtain the pair distribution function for the quantum particles,

$$\begin{aligned} G(\mathbf{r},\mathbf{r}') &= g(\mathbf{r},\mathbf{r}') - \frac{1}{n^2}\langle\psi^\dagger(\mathbf{r})\psi(\mathbf{r})\rangle\delta(\mathbf{r}-\mathbf{r}') \\ &= \frac{1}{n^2}\langle\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})\rangle. \end{aligned} \tag{13.3.8}$$

The given boson system is translationally invariant. The distribution function can be simplified to depending only on the relative distance between the pair of particles,

$$G(\mathbf{r}-\mathbf{r}') = \frac{1}{n^2}\langle\psi^\dagger(\mathbf{r}-\mathbf{r}')\psi^\dagger(0)\psi(0)\psi(\mathbf{r}-\mathbf{r}')\rangle. \tag{13.3.9}$$

Wick's theorem states that the non-interacting N-particle state expectation value of a "normal" product of equal numbers of creation and annihilation operators can be broken into a sum of products of expectation values of all possible pairs of one creation and one annihilation operator. Thus, the pair distribution function becomes

$$G(\mathbf{r}) = \frac{1}{n^2}[\langle\psi^\dagger(\mathbf{r})\psi(\mathbf{r})\rangle\psi^\dagger(0)\psi(0)\rangle + \langle\psi^\dagger(\mathbf{r})\psi(0)\rangle\langle\psi^\dagger(0)\psi(\mathbf{r})\rangle]. \tag{13.3.10}$$

(For fermions, the second term would be negative because an odd number of pair exchanges were made.)

Since the translation invariance of the system ensures that $\langle\psi^\dagger(\mathbf{r})\psi(\mathbf{r})\rangle = n$ is independent of the position, the pair distribution function is

$$G(\mathbf{r}) = 1 + \left|\frac{n_1(0,\mathbf{r})}{n}\right|^2, \tag{13.3.11}$$

where $n_1(0,\mathbf{r}) = \langle\psi^\dagger(0)\psi(\mathbf{r})\rangle$ is known as the one-particle reduced density matrix. By means of the plane-wave expansion (13.3.3), it is

$$\langle\Psi|\psi^\dagger(0)\psi(\mathbf{r})|\Psi\rangle = V^{-1}\sum_{\mathbf{k}} n_k e^{i\vec{k}\cdot\vec{r}}, \tag{13.3.12}$$

which can be evaluated explicitly, for example, for a Boltzmann distribution (as a high temperature approximation for the bose thermal distribution),

$$n_k = e^{-(\epsilon_k-\mu)/k_BT}, \tag{13.3.13}$$

as

$$G(r) = 1 + e^{-r^2/\lambda_T^2}, \tag{13.3.14}$$

where λ_T is the thermal wavelength, $\hbar/\sqrt{mk_BT}$. Note that at $r = 0$ the pair function is 2 and it decays off to unity. The enhancement of the probability of finding one boson on top of another (even without interaction) is the constructive interference effect of the two boson wave functions. This bunching effect is found in a beam of photons in thermal equilibrium by the intensity interferometry of Hanbury Brown and Twiss, which will be studied in the next chapter on the quantization of the electromagnetic field.

13.3.3 Verification of the special case of Wick's theorem

In the plane-wave expansion, the pair distribution function becomes,

$$n^2G(\mathbf{r}) = V^{-2}\sum_{klmn} e^{-i\vec{k}\cdot\vec{r}+i\vec{n}\cdot\vec{r}}\langle\Psi|c^\dagger_{\mathbf{k}}c^\dagger_{\mathbf{l}}c_{\mathbf{m}}c_{\mathbf{n}}|\Psi\rangle. \tag{13.3.15}$$

For nonzero expectation values, the states $\mathbf{k}$ and $\mathbf{l}$ must pair up with the states $\mathbf{m}$ and $\mathbf{n}$. Because of the boson nature, the values are different depending on whether $\mathbf{k}$ and $\mathbf{l}$ are the same or not. Thus,

$$\langle\Psi|c^\dagger_{\mathbf{k}}c^\dagger_{\mathbf{l}}c_{\mathbf{m}}c_{\mathbf{n}}|\Psi\rangle = (1-\delta_{\mathbf{k},\mathbf{l}})(\delta_{\mathbf{k},\mathbf{n}}\delta_{\mathbf{l},\mathbf{m}} + \delta_{\mathbf{k},\mathbf{m}}\delta_{\mathbf{l},\mathbf{n}})n_{\mathbf{k}}n_{\mathbf{l}} + \delta_{\mathbf{k},\mathbf{l}}\delta_{\mathbf{k},\mathbf{m}}\delta_{\mathbf{k},\mathbf{n}}n_{\mathbf{k}}(n_{\mathbf{k}}-1). \tag{13.3.16}$$

When the expectation value is put back in the sum, the factor $\delta_{\mathbf{k},\mathbf{l}}$ restricting the terms on the right makes the contribution from such terms smaller than those terms without such restriction by a factor of $1/N$. Thus, in the large N or V limit keeping the density constant,

$$\langle\Psi|c^\dagger_{\mathbf{k}}c^\dagger_{\mathbf{l}}c_{\mathbf{m}}c_{\mathbf{n}}|\Psi\rangle = (\delta_{\mathbf{k},\mathbf{n}}\delta_{\mathbf{l},\mathbf{m}} + \delta_{\mathbf{k},\mathbf{m}}\delta_{\mathbf{l},\mathbf{n}})n_{\mathbf{k}}n_{\mathbf{l}}. \tag{13.3.17}$$

This is an example of Wick's theorem of two possible pairings,

$$\langle c^\dagger_{\mathbf{k}}c^\dagger_{\mathbf{l}}c_{\mathbf{m}}c_{\mathbf{n}}\rangle = \langle c^\dagger_{\mathbf{k}}c_{\mathbf{n}}\rangle\langle c^\dagger_{\mathbf{l}}c_{\mathbf{m}}\rangle + \langle c^\dagger_{\mathbf{k}}c_{\mathbf{m}}\rangle\langle c^\dagger_{\mathbf{l}}c_{\mathbf{n}}\rangle. \tag{13.3.18}$$

13.4 Hartree and Fock Approximations in a Fermion System

In the rest of this chapter, we shall concentrate on the many-fermion system. The simplest approximation to find the ground-state energy is by utilizing the variational principle starting with the wave function of a system of noninteracting fermions, i.e., N particles occupying the single-particle states $\{\phi_j(r)\}$, where $j = 1, \ldots, N$. The "best" single-particle wave functions are defined as those minimizing the total energy of the whole system.

By the method in the last chapter, we would write down the Hamiltonian of the system of fermions,

$$H = \sum_j \left[\frac{p_j^2}{2m} + v(r_j)\right] + \frac{1}{2}\sum_{j\neq k} u(r_j - r_k), \tag{13.4.1}$$

where v is the one-particle potential and u is the interaction between two particles. To find the ground state energy, we minimize the energy expectation $\langle\Psi|H|\Psi\rangle$, where $|\Psi\rangle$ is a Slater determinant of N single particle orbitals $\phi_j(r)$. The resultant variational equations then govern the orbitals.

As an alternative way to proceed, we shall evaluate the energy by the second-quantization method. We let the annihilation operator be given by the infinite series,

$$\psi(r) = \sum_{j=1}^{\infty} \phi_j(r) c_j. \tag{13.4.2}$$

The spin degrees of freedom are understood to be included in the coordinates $r = (\mathbf{r}, m_s)$ and the quantum numbers $j = (\mathbf{k}, \sigma)$. The single-particle functions $\phi_j(r)$ are to be determined below.

The Hamiltonian for the whole system in second quantized form is

$$\begin{aligned} H &= \int dr \psi^\dagger(r)\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi(r) + \int dr \psi^\dagger(r) v(r)\psi(r) \\ &+ \frac{1}{2}\int dr \int dr' \psi^\dagger(r)\psi^\dagger(r') u(r - r')\psi(r')\psi(r). \end{aligned} \tag{13.4.3}$$

The first term on the right is the kinetic energy. The second is the total potential energy due to the external potential $v(r)$ acting on each particle. For example, in an atom, molecule, or solid, $v(r)$ is the Coulomb potential due to the positively charged nuclei, which are taken to remain fixed in position. The third term is the interaction between pairs of particles, for example, the Coulomb repulsion between electrons,

$$u(r-r') = \frac{e^2}{4\pi\epsilon_0|r-r'|}. \tag{13.4.4}$$

In terms of the annihilators c_j, the Hamiltonian is

$$H = \sum_{j,k} h_{jk} c_j^\dagger c_k + \frac{1}{2}\sum_{ijk\ell} u_{ijk\ell} c_i^\dagger c_j^\dagger c_k c_\ell, \tag{13.4.5}$$

where the single-particle part of the energy is given by the matrix element

$$h_{jk} = \int dr \phi_j^*(r)\left[-\frac{\hbar^2}{2m}\nabla^2 + v(r)\right]\phi_k(r), \tag{13.4.6}$$

and the interaction part is given by the Coulomb matrix element,

$$u_{ijk\ell} = \int dr \int dr' \phi_i^*(r)\phi_j^*(r')u(r-r')\phi_k(r')\phi_\ell(r). \tag{13.4.7}$$

The variational ground-state vector is

$$|\Psi\rangle = \prod_{j=1}^{N} c_j^\dagger|0\rangle, \tag{13.4.8}$$

and its wave function is the $N \times N$ Slater determinant,

$$\langle r_1,\ldots,r_N|\Psi_0\rangle = \frac{1}{\sqrt{N!}}\text{det}[\phi_j(r_{j'})]. \tag{13.4.9}$$

The energy expectation is

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{13.4.10}$$

The Hamiltonian matrix element is easily evaluated if one has a couple of relations. One is

$$\langle\Psi|c_j^\dagger c_k|\Psi\rangle = n_j\delta_{jk}, \tag{13.4.11}$$

where $n_j = 1$ if state j is occupied by a particle and $= 0$ if it is unoccupied. Note that if k is not one of the states in $|\Psi\rangle$, the state will be annihilated. The reason $j = k$ follows from the orthogonality of two N-particle states with different orbitals. The other is

$$\langle\Psi|c_i^\dagger c_j^\dagger c_k c_\ell|\Psi\rangle = n_i n_j(\delta_{i\ell}\delta_{jk} - \delta_{ik}\delta_{j\ell}), \tag{13.4.12}$$

which can be evaluated by the same pairing reasoning of each annihilation operator with a creation operation as in the bose case above. Note the minus sign which comes with the permutation required before the pairing. Hence, the variational energy is

$$E = \sum_j h_{jj} + \frac{1}{2}\sum_{ij} n_i n_j (u_{ijji} - u_{ijij}), \tag{13.4.13}$$

as we have taken the single-particle orbitals to be orthonormal. Since the matrix elements of h and u involve the functions $\phi_j(r)$ and $\phi_j^*(r)$, we may vary them independently to find the smallest E. Since

$$\langle\Psi|\Psi\rangle = \prod_{j=1}^{N}\int dr\, \phi_j^*(r)\phi(r), \tag{13.4.14}$$

we use the Lagrange multipliers ϵ_j to keep the single-particle wave functions normalized and minimize

$$\langle\Psi|H|\Psi\rangle - \sum_{j=1}^{N}\epsilon_j\int dr\, \phi_j^*(r)\phi(r), \tag{13.4.15}$$

subject to the condition that

$$\int dr\, \phi_j^*(r)\phi(r) = 1, \qquad \text{for all } j. \tag{13.4.16}$$

The variational equations can be obtained by differentiating Eq. (13.4.13) with respect to $\phi^*(r)$,

$$-\frac{\hbar^2}{2m}\nabla^2\phi_j(r) + \int dr'\, v_{\text{eff}}(r,r')\phi_j(r') = \epsilon_j\phi_j(r), \tag{13.4.17}$$

where

$$v_{\text{eff}}(r,r') = v(r)\delta(r-r') + v_H(r)\delta(r-r') + v_x(r,r'), \tag{13.4.18}$$

$$v_H(r) = \sum_i n_i \int dr'\, u(r-r')|\phi_i(r')|^2, \tag{13.4.19}$$

$$v_x(r,r') = -\sum_i n_i\phi_i(r)u(r-r')\phi_i^*(r'). \tag{13.4.20}$$

The result can be simply interpreted as that the Hartree-Fock approximation to the ground state is made up of N fermions in the orbitals $\{\phi_j(r)\}$, which are governed by the one-particle

Schrödinger equation with an effective non-local potential v_{eff}. The effective potential is composed of three terms. The first is, of course, the original external potential $v(r)$. The second $v_H(r)$ is the potential due to interaction of the particle in orbital j with the density distribution of *all* the particles. For electrons, this is the electrostatic potential due to the particle density $n(r)$,

$$v_H(r) = \int dr'\, u(r-r')n(r'), \tag{13.4.21}$$

$$n(r') = \sum_i n_i |\phi_i(r')|^2. \tag{13.4.22}$$

It might seem that the electrostatic interaction of an orbital j with itself is unphysical and should be excluded from the sum above. Indeed, the original Hartree approximation, which is a variational result using the trial wave function of a product of N orbitals (without anti-symmetrization), leads to the Hartree potential $v_H(r)$ with the sum excluding the $i = j$ term. However, for the convenience which an orbital-independent potential brings, we have kept the self-interaction term in the Hartree potential. The defect is ameliorated in two different ways: (1) the second sum also contains an $i = j$ term which cancels out the first term and (2) in very large systems, the error is of the order $1/N$.

The third term in the effective potential, $v_x(r, r')$, is the only nonlocal term. It is known as the Fock term or the exchange potential. Notice that from Eq. (13.4.13) the Hartree term u_{ijji} originates in the Coulomb matrix element $u_{ijk\ell}$ which causes the scattering of one particle from state ℓ to state i (see Eq. (13.4.12)) via interaction with a second particle from state k to state j. The term "exchange" comes from the exchange of the roles of states k and ℓ in the two-particle scattering. This point is illustrated in Fig. 13.1.

If we consider the fermions to be spin 1/2-particles, the states i and j contain spin up and down states. Further, let us consider the interaction potential to be independent of spins, as is the case for the Coulomb interaction, i.e. in $u_{ijk\ell}$, states i and ℓ have the same spin states and so do j and k. The sum over i in the density $n(r)$ includes sum over spin up and down states and the Hartree potential for the electron in state j depends equally on the density distribution of both types of spin states. On the other hand, while the so-called reduced or one-particle density matrix $n(r, r') = \sum_i n_i \phi_i(r)\phi_i^*(r')$ does sum over both spin states, the exchange

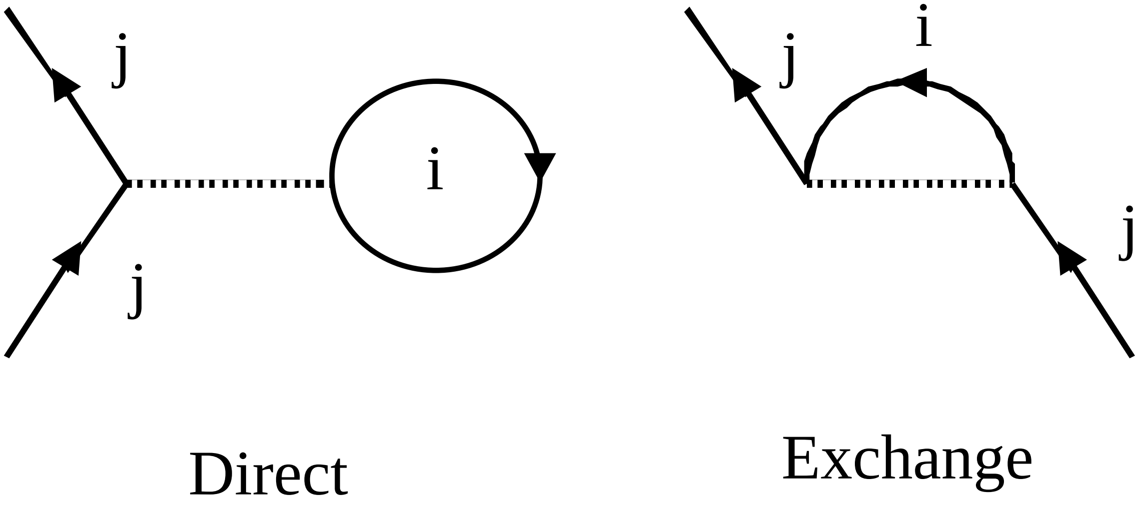

Figure 13.1: Direct and exchange interaction between two particles. The solid lines with arrows represent the propagation of the two particles and the dashed line the interaction. The diagram on the left represents the matrix element u_{jiij} in Eq. (13.4.7) and the diagram on the right is the exchange counterpart u_{jiji}. Note the sequence of the indices start from the upper left corner of the diagram and goes clockwise.

potential which contains the scattering of a particle from state i to j, leading to these two states having the same spin state. (This is clear from Fig. 13.1.) The repulsive nature of the exchange potential tends to keep the fermions with parallel spins away from each other. This is the result of the Pauli exclusion principle obeyed by the variational determinant.

Unlike the old one-particle Schrödinger equation, the effective potential in the Hartree-Fock equation depends on the one-particle density matrix and, thus, on the wave function we need to solve. The solution is usually carried out by iteration. The potential is then said to be selfconsistent. The local part, $v + v_H$, is sometimes called the self-consistent potential.

The Hartree-Fock approximation does a fair job in calculating the total energy of the electrons in atoms and the electronic configurations of the atoms in the periodic table. The relative ordering of the 3d and 4f electrons and other similar shells tends to be less reliable. While the accuracy of one per cent for the total energy by the Hartree-Fock approximation seems impressive, this discrepancy, which is called the correlation energy, is important for molecule bonds and solid cohesion. The most important part of the correlation effect is the repulsion by the electrons of opposite spins beyond the Hartree potential, which is not in the exchange potential.

A model of a simple metal is given by a system of interacting electrons in a uniform background of fixed positive charges, with the amount of charge neutralizing the charge of N electrons. The system is known as the homogeneous electron gas or the jellium. Problem 11 shows what the Hartree-Fock solutions are. Because of the complete translational symmetry of the Hamiltonian, the Hartree-Fock orbitals are plane waves. The ground state energy can be split into a kinetic energy term and a Fock or exchange term. Because of the compensation effect of the positive background and the electron gas, there is zero contribution from the Hartree term plus the potential energy due to the positive background charges. To compare the Hartree-Fock energy with experiment, we need to take simple metals such as the alkali metals or aluminum and subtract out the electrostatic energy (including the Hartree term). Then, the result is not as good as for atoms, especially for lower density metals. A particularly egregious error is that the Fermi velocity (see Problem 11) is infinite. The difference between the exact energy and the Hartree-Fock energy is known as the correlation energy of the homogenous electron gas. Note that the kinetic energy in the Hartree-Fock approximation is not the exact kinetic energy. Therefore, the correlation energy contains a part which is a correction to the kinetic energy as well as a part which is a correction to the interaction energy. The theory of the correlation effects is beyond the scope of this text and the reader is referred to [13].

13.5 Density Functional Theory

The density functional theory provides an alternate view to the Schrödinger equation where the potential is the key to the determination of the properties of the system. It has a long history starting with the Thomas-Fermi approximation and the Dirac exchange correction in the early days of quantum theory. The general formulation and modern applications started in the sixties. The method has been developed into a widely used computational tool for the studies of the electronic and structural properties of molecules and solids.

For simplicity of exposition, we shall now restrict ourselves to the consideration of a system of electrons which interact with each other via the Coulomb repulsion and with nuclei in a fixed configuration. This then applies to a wide range of systems from atoms to molecules to condensed matter. It is also possible to extend the theory to other fermions, particularly systems of nucleons, and to interacting bosons.

The Hamiltonian of our many-electron system is given by

$$\hat{H} = \hat{T} + \hat{V} + \hat{U}, \tag{13.5.1}$$

where the kinetic energy term is

$$\hat{T} \;=\; \int dr\, \psi^\dagger(r) \left(-\frac{\hbar^2}{2m}\right) \nabla^2 \psi(r), \tag{13.5.2}$$

the potential energy in the presence of a fixed constellation of nuclei is

$$\hat{V} \;=\; \int dr\, \psi^\dagger(r) v(r) \psi(r), \tag{13.5.3}$$

and the mutual Coulomb repulsion between the electrons is

$$\hat{U} = \frac{1}{2} \int dr \int dr' \psi^\dagger(r) \psi^\dagger(r') u(r,r') \psi(r') \psi(r) \tag{13.5.4}$$

We have seen that the Hartree-Fock approximation falls short in the physical and chemical properties which depend on the correlation effects. An improvement is to use linear combination of the Slater determinants, known as the configuration interaction method. However, the complexity of the computation grows exponentially with the size of the system. For extensive systems, especially metals, the model of homogeneous electron gas is studied for its interaction effects. (See Sec. 13.5.6 and Problem 11).

The density functional theory provides an alternative way to proceed. First, the electron density distribution replaces the many-electron wave function as conceptually the key quantity to compute. Historically, this point of view started with the Thomas-Fermi approximation. Second, the theory provides an approximation which makes use of the properties of the homogeneous electron gas which are known. After much testing in thirty some years, the strengths and weaknesses of the approximation are pretty well known.

13.5.1 The density functional theorem or Hohenberg-Kohn theorem

All properties of an interacting electron system is a functional of the density distribution.

Let us elaborate on the statement of the theorem. In the Hamiltonian of the interacting electron system, we observe three inputs which determine the properties of the system, the electron mass, the Coulomb interaction between two electrons and the external potential $v(r)$. If we consider the class of all many-electron systems which include atoms, molecules, liquids, and solids, the electron mass and the interaction potential between two electrons are constant throughout the class but each external potential $v(r)$ uniquely determines all the properties of a particular system. In principle, once the potential is given, the Schrödinger equation for the system may be solved for the energy eigenfunctions and any property calculated. Thus, we say a property is a functional of the potential $v(r)$. The word "functional" is used in place of "function" because the variable is not a number but a function itself. In particular, the electron ground-density density distribution

$$n(r) = \langle \Psi | \psi^\dagger(r) \psi(r) | \Psi \rangle, \tag{13.5.5}$$

is a functional of the potential. The Density Functional Theorem asserts that the converse is also true, namely that the potential is, apart from an arbitrary constant, uniquely determined by the density $n(r)$.

The proof is simple, showing, by *reductio ad absurdum*, that no two potentials differing by more than a constant can correspond to the same density distribution. Suppose that there are two potentials $v(r)$ and $v'(r)$ which differ by more than a constant and which produce the same density $n(r)$. Aside from $n(r)$, all other quantities associated with the system with potential $v'(r)$ are denoted by primed symbols. From the variational principle we have the ground-state energy

$$E = \langle \Psi | H | \Psi \rangle \leq \langle \Psi' | H | \Psi' \rangle, \tag{13.5.6}$$

where Ψ and Ψ' are the ground states of the systems with potentials $v(r)$ and $v'(r)$, respectively. The equality is excluded in Eq. (13.5.6). Were the equality to hold, Ψ' would be another state of H of the same energy as the ground state and

$$(\hat{V} - \hat{V}')|\Psi'\rangle = (E - E')|\Psi'\rangle. \tag{13.5.7}$$

It would mean that the wave function had to vanish where the potentials differ which is impossible unless they differ only by a constant.

The last expression of Eq. (13.5.6) is

$$\langle\Psi'|H|\Psi'\rangle = \langle\Psi'|H' + (\hat{V} - \hat{V}')|\Psi'\rangle = E' + \int dr[v(r) - v'(r)]n(r). \qquad (13.5.8)$$

Hence, the inequality (13.5.6) becomes

$$E < E' + \int dr[v(r) - v'(r)]n(r). \qquad (13.5.9)$$

Interchanging the roles of the two systems, we have

$$E' < E + \int dr[v'(r) - v(r)]n(r). \qquad (13.5.10)$$

Addition of the two inequalities lead to the absurd result that $E + E' < E' + E$.

When the theorem was first published, there were many objections from the physics and chemistry communities. One reason was that it was then known that the knowledge of one-particle density matrix $n(r, r')$ was sufficient to determine all the properties of the interacting system. Since the density is only the diagonal part of the density matrix, it contains less information than the density matrix. How could it then replace the density matrix? A simple and familiar way is to view the change of the functional variable from the potential $v(r)$ to the density $n(r)$ as analogous to the Legendre transformation in thermodynamics when the ground-state energy as a functional of v contains the potential energy term

$$V \equiv \langle\Psi| \int dr\, \psi^\dagger(r)v(r)\psi(r)|\Psi\rangle = \int drn(r)v(r), \qquad (13.5.11)$$

which is a “product” of v and n, similar to the PV, TS or MH term in the free energy in thermodynamics.

As a corollary of the theorem, since $v(r)$ is a functional of $n(r)$, every property of the electron system is and, in particular, so are the ground-state expectation values of the kinetic energy and interaction energy.

Clearly, the theorem can be applied to more than the class of electron systems. It could be for a class of fermions or of bosons. In the way the theorem was stated above, the mathematical niceties of the Banach spaces of $n(r)$ and of $v(r)$ are glossed over. A constructive procedure which avoids such problems to some extent was given by Levy.

As a result of the density functional theorem, the ground-state energy can be put in the form:

$$E \equiv E[v,n] = \int dr n(r) v(r) + F[n(r)] \tag{13.5.12}$$

where the first term is the ground-state expectation of V and $F[n]$ is the expectation value of $T+U$, the kinetic energy and interaction energy. If the electrostatic energy due to the static electron charge distribution $-en(r)$ is explicitly written out,

$$F[n] = \frac{1}{2}\int dr \int dr' n(r) u(r-r') n(r') + G[n]. \tag{13.5.13}$$

The energy functional G can further be expressed in terms of the one-particle density matrix

$$n(r,r') = \langle\Psi|\psi^\dagger(r')\psi(r)|\Psi\rangle, \tag{13.5.14}$$

and the two-particle correlation function

$$c(r,r') = \langle\Psi|\psi^\dagger(r)\psi^\dagger(r')\psi(r')\psi(r)|\Psi\rangle - n(r)n(r'), \tag{13.5.15}$$

which is related to the pair distribution function. Hence,

$$G[n] = \int dr g(r,[n]), \tag{13.5.16}$$

$$g(r,[n]) = -\frac{\hbar^2}{2m}\nabla^2 n(r,r') \mid_{r'=r} + \frac{1}{2}\int dr' u(r') c(r-\frac{1}{2}r', r+\frac{1}{2}r'). \tag{13.5.17}$$

For later use, we have introduce the energy density $g(r,[n])$ which is a local function of r as well as a functional of the density $n(r)$.

13.5.2 The variational theorem with respect to the density

If another density $n'(r)$ which corresponds to the system with the potential $v'(r)$ which differs by more than a constant from $v(r)$, the substitution of $n'(r)$ in Eq. (13.5.12) will yield an energy larger than the ground state energy.

As before, we have

$$\langle\Psi|H|\Psi\rangle < \langle\Psi'|H|\Psi'\rangle. \tag{13.5.18}$$

But the right-hand side is

$$\langle\Psi'|H|\Psi'\rangle = \langle\Psi'|\hat{V}|\Psi'\rangle + \langle\Psi'|\hat{T}+\hat{U}|\Psi'\rangle = \int drv(r)n'(r) + F[n']. \qquad (13.5.19)$$

Hence,

$$E_v[n] < E_v[n']. \qquad (13.5.20)$$

For a given potential $v(r)$, the correct density put in Eq. (13.5.12) yields the lowest energy.

The variational theorem can be put in an alternative form. Let $\delta n(r)$ be a small deviation from the correct density distribution $n(r)$ without changing the total number of particles, $\int dr\delta n(r) = 0$. The first-order change in energy is zero,

$$\delta E_v[n] = 0. \qquad (13.5.21)$$

Combining this equation with the condition of constant number by means of a Lagrange multiplier μ leads to

$$\delta E_v[n] - \mu \int dr\delta n(r) = 0. \qquad (13.5.22)$$

A physical interpretation for μ is the chemical potential, i.e. the energy required to remove or add an electron in an extensive (or thermodynamic) system. From the definition of the functional derivative as

$$F[n+\delta n] - F[n] = \int dr \frac{\delta F}{\delta n(r)}\delta n(r) + O((\delta n)^2), \qquad (13.5.23)$$

Eq. (13.5.12) yields

$$\frac{\delta F}{\delta n(r)} + v(r) = \mu. \qquad (13.5.24)$$

This functional differential equation in principle determines the density distribution.

The two theorems form the theory framework for an approach to the problem of the inhomogeneous interaction electron system. Instead of the usual way of attempting to construct the ground-state wave function, we let the electron density distribution play the central role to characterize the system. The task is first to construct the functional $F[n]$, i.e. the functional dependence of the kinetic plus interaction energy on the density $n(r)$. In what follows, we shall examine a number of ways to construct $F[n]$. Once $F[n]$ is at hand, one can then try to solve the variational equation.

The most obvious approximation is to find the infinite series in powers of $v(r)$ and convert it to a series in powers of $n(r) - n_0$. In practice, this is not a good computational scheme but it is useful in contemplating some structures of the theory, such as in showing the existence of the density functional for a set of the density functions near a constant density.

13.5.3 Systems of noninteracting fermions

The density functional theory certainly applies to the many-fermion systems without interaction. This is more than an exercise to orient ourselves with the density functional theory. It can actually tell us what is missing in the interaction effects and also provide a handle to solve the bland-looking functional differential equation (13.5.24). The sum of the single-particle energies provides the ground-state energy in the density-functional form

$$E_s = \int drv(r)n(r) + T_s[n], \tag{13.5.25}$$

where $T_s[n]$ denotes the kinetic energy of the noninteracting fermion system with the density $n(r)$. The variational equation which determines the density is

$$\frac{\delta T_s}{\delta n(r)} + v(r) = \mu. \tag{13.5.26}$$

Although we do not know if the variational equation has more than one solution for the density, we do know that it has at least one, given by solving the single-particle Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(r)\right]\phi_j(r) = \varepsilon_j\phi_j(r), \tag{13.5.27}$$

and constructing the density distribution

$$n(r) = \sum_j \theta(\mu - \varepsilon_j)|\phi(r)|^2. \tag{13.5.28}$$

We have this rather useful result that a functional differential equation of the form of Eq. (13.5.26) can be solved by the associated one-particle Schrödinger equation. Now we just need to mangle an energy functional into the form of Eq. (13.5.25). This observation enables us to avoid the unpleasant task of having to construct $T_s[n]$, although in some circumstances it is possible to do so. The construction of the perturbation series in powers of the potential $v(r)$ for the noninteracting case is easier than the interacting case mentioned in the last subsection. The power series of T_s in $v(r)$ is then inverted to a power series of $T_s[n]$ in terms of $n(r)-n_0$, the deviation of the density about the average.

13.5.4 The self-consistent field approximation

In the spirit of the Hartree approximation we make the approximation for the functional $F[n]$ by keeping just the electrostatic interaction energy term,

$$F[n] = \frac{1}{2}\int dr \int dr' n(r)u(r-r')n(r') + T_s[n]. \tag{13.5.29}$$

The variational equation is then

$$\frac{\delta T_s}{\delta n(r)} + v(r) + v_H(r) = \mu. \tag{13.5.30}$$

By the argument in the last subsection, the solution for the density is given by solving the selfconsistent field equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{scf}(r)\right]\phi_j(r) = \varepsilon_j\phi_j(r), \tag{13.5.31}$$

where the self-consistent field potential is

$$v_{scf}(r) = v(r) + v_H(r). \tag{13.5.32}$$

Compare this with the results in the section on the Hartree and Fock approximations.

13.5.5 The density functional equation

The previous two subsections give us a way to develop the density functional theory further. Let us write

$$G[n] \equiv T_s[n] + E_{xc}[n]. \tag{13.5.33}$$

The ground-state energy is now split up into

$$E = T_s[n] + \int dr v(r)n(r) + \frac{1}{2}\int dr \int dr' n(r)u(r-r')n(r') + E_{xc}[n], \quad (13.5.34)$$

i.e., the kinetic energy of noninteracting fermions which have the same density $n(r)$, the potential energy due to the external potential, the electrostatic interaction energy, and the energy beyond the Hartree energy. Thus, we follow the common usage of naming $E_{xc}[n]$ as the exchange and correlation energy. We note that

$$T_s[n] \neq \langle\Psi|\hat{T}|\Psi\rangle, \quad (13.5.35)$$

i.e., the kinetic energy of the noninteracting system is **not** equal to the true kinetic energy of the ground state of the interacting system with the same density distribution.

The variational equation becomes

$$\frac{\delta T_s}{\delta n(r)} + v_{eff}(r) = \mu. \quad (13.5.36)$$

The effective potential has three terms:

$$v_{eff}(r) = v(r) + v_H(r) + v_{xc}(r). \quad (13.5.37)$$

The new term,

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}, \quad (13.5.38)$$

is the exchange-correlation potential. It is a local function of r and a functional of the density. For simplicity, the functional dependence of v_H, v_{xc} and v_{eff} is understood.

The density is then given by

$$n(r) = \sum_j \theta(\mu - \varepsilon_j)|\phi_j(r)|^2. \quad (13.5.39)$$

where the orbitals are the solutions of the density functional equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\right]\phi_j(r) = \varepsilon_j\phi_j(r). \quad (13.5.40)$$

Note that the reduction of the solution of a many-body problem to the solution of an effective one-particle Schrödinger equation is exact. The theory concentrates the work involved in including the exchange and correlation effects into the construction of $v_{xc}(r)$.

13.5.6 The gradient expansion

As a preparation for an approximation of the exchange-correlation potential which turns out to be widely used, let us consider an approximation dated back to Thomas and Fermi. The density functional theory is also a very natural framework for the Thomas-Fermi approximation and its extensions.

Imagine that the spatial variation of the density is actually slowly varying. Then, in a neighborhood of the point r, we might approximate first the local properties of the system as a function of the local density $n(r)$. The energy density in Eq. (13.5.17) for the homogeneous gas is then given by

$$g_0(n) = n\varepsilon_h(n), \tag{13.5.41}$$

where $\varepsilon_h(n)$ is the total energy per electron of the homogenous electron gas. It can be broken up into three parts

$$\varepsilon_h(n) = \varepsilon_0(n) + \varepsilon_x(n) + \varepsilon_c(n). \tag{13.5.42}$$

The first two terms are the noninteracting part of the kinetic energy and the exchange energy, given by

$$\begin{aligned}
\varepsilon_0(n) &= \frac{3\hbar^2}{10m}(3\pi^2 n)^{2/3} = \frac{1.1050}{r_s^2} \text{ a.u.}, && (13.5.43)\\
\varepsilon_x(n) &= -\frac{3e^2}{4\pi}(3\pi^2 n)^{1/3} = -\frac{0.4582}{r_s} \text{ a.u.}, && (13.5.44)
\end{aligned}$$

where r_s is the mean distance of the electron in units of the Bohr radius given in terms of the density by $n = 3/(4\pi r_s^3 a_0^3)$. (See Problem 11.) The correlation energy was first considered by Wigner [29] in the low density limit and an interpolation formula was given with correction by [19],

$$\varepsilon_c(n) = -\frac{0.44}{r_s + 7.79} \text{ a.u.}. \tag{13.5.45}$$

The correlation energy $\varepsilon_c(n)$ has been evaluated as a function of the constant electron density [4]. The method is based on a variational wave function which contains two-particle correlation (the Jastrow function). A convenient form of the result may be written as an analytical formula [17]:

$$\begin{aligned}\varepsilon_c(n) &= -\frac{0.1423}{1+1.0529\sqrt{r_s}+0.3334r_s}, \text{ for } r_s \geq 1; \qquad (13.5.46)\\ &= -0.0480+0.0311\ln r_s - 0.0116r_s + 0.0020r_s\ln r_s, \text{ for } r_s \leq 1.\end{aligned}$$

Thus, we can consider the total energy per electron as a function of density as known.

If the density distribution actually varies gently over space, the first approximation for the energy functional is

$$G[n] = \int drn(r)\varepsilon_h(n(r)). \qquad (13.5.47)$$

The classic Thomas-Fermi approximation keeps only the kinetic energy term in Eq. (13.5.43). The variational equation becomes

$$\mu_h(n(r)) + v_(r) + v_H(r) = \mu, \qquad (13.5.48)$$

where

$$\mu_h(n) = \frac{d}{dn}[n\varepsilon_h(n)] \qquad (13.5.49)$$

is the chemical potential of the homogeneous gas at the density n. When the potential $v(r)$ is given, the variational equation may be solved selfconsistently for the density $n(r)$.

To improve on the local approximation, one would include the effects of the gradient of the density. The gradient expansion of the energy density has the form

$$\begin{aligned}g(r,[n]) &= g_0(n(r)) + \sum_\alpha g_1^\alpha(n(r))\frac{\partial}{\partial r_\alpha}n(r) \qquad (13.5.50)\\ &+ \sum_{\alpha,\beta}\left[g_{1,1}^{\alpha,\beta}(n(r))\frac{\partial}{\partial r_\alpha}n(r)\frac{\partial}{\partial r_\beta}n(r) + g_2^{\alpha,\beta}(n(r))\frac{\partial^2}{\partial r_\alpha\partial r_\beta}n(r)\right] + \ldots.\end{aligned}$$

Rotational symmetry excludes the odd-power gradient terms and simplifies the expression to

$$g(r,[n]) = g_0(n(r)) + g_{1,1}(n(r))|\nabla n(r)|^2 + \ldots. \qquad (13.5.51)$$

We have also eliminated the term $g_2(n(r))\nabla^2 n(r)$ since it can be expressed as a divergence plus terms linear in $\nabla n(r)$.

Application of the Thomas-Fermi approximation to the atoms has given a good trend for variation of some properties of atoms as functions of the atomic number. However, the density reflects too faithfully the features of the potential. Thus, it diverges at the nucleus. The density also lacks the shell structure. Piecemeal addition of the gradient correction terms yields results which oscillate about the true solution.

13.5.7 The local-density approximation

Since the quantum effects on the density are retained approximately in the Hartree approximation, retention of the kinetic part, $T_s[n]$, should be a vast improvement over the Thomas-Fermi approximation. The problem now becomes the construction of the exchange-correlation energy functional $E_{xc}[n]$. A simple approximation in the spirit of the Thomas-Fermi approximation is the local-density approximation:

$$E_{xc} = \int dr \varepsilon_{xc}(n(r))n(r), \tag{13.5.52}$$

where $\varepsilon_{xc}(n)$ is the exchange-correlation energy per electron of the homogeneous gas at the density n. The exchange-correlation potential is then given by

$$v_{xc} = \mu_{xc}(n) \equiv \frac{d}{dn}[n\epsilon_{xc}(n)], \tag{13.5.53}$$

the exchange-correlation part of the chemical potential of the homogeneous electron gas at the local density n. Gradient corrections have also been given in the literature.

The many-electron problem is now reduced to solving the one-particle Schrödinger equation (13.5.40) with the effective potential in the local-density approximation,

$$v_{LDA}(r) = v(r) + v_H(r) + \mu_{xc}(n(r)). \tag{13.5.54}$$

This was first tried out on a number of atoms [25]. The comparison of a number of properties with experiment and with the Hartree-Fock approximation was quite encouraging and the amount of computation, being similar to the Hartree approximation, was considerably less than the Hartree-Fock approximation. Since then, many calculations with vastly larger scale problems have been carried out by many workers, particularly in quantum chemistry and in solid state physics. The results have been very useful as guides to experiments and to interpretation of experiments. There are also sufficient defects in the local-density approximation to keep this field an active research area.

13.5.8 Summary

WHAT IS DENSITY FUNCTIONAL THEORY?

The one-line answer is that it is many-body quantum mechanics for everybody. By expressing the ground-state energy as a functional of the density, the theory reduces the many-body problem to an equivalent one-particle theory with all the many-body effects collected in an effective potential. In this form, simple and effective approximation for including the many-body effects can be devised.

Although I have not explicitly mentioned it in this section, the spin-dependence is implicit in r and could be included explicitly in the spin-polarized cases or implicitly in the spin-compensated cases. Extension to systems at final temperature is also possible. Extensions to other fermion and boson systems have also been made. The wide range of applications possible is clearly outside the scope of this introductory account. The reader is referred to the extensive literature.

13.6 Theory of Superconductivity

The superconducting ground state of a system of fermions with a mutual attractive interaction, known as the BCS state, is made up of pairs of fermions (known as the Cooper pairs). The state owns its very existence to the interaction. It is the foundation of a theory of the striking properties of the superconductors for their electric conduction without resistance, perfect diamagnetism, and unusual electromagnetic properties. The pairing state is also valuable in understanding the distinct nature of the nuclei with even number of nucleons compared with the odd-number ones. The concept of BCS pairing and the deduced vortices are also applied to elementary particle theory, such as the chiral symmetry breaking by the condensation of particle-antiparticle pair or the spontaneous symmetry breaking in the Higgs sector by quark-antiquark pair condensation. Strictly speaking, these latter condensations are closer to the electron-hole condensation in solids giving rise to charge density waves, whose theory was first given by Fröhlich. We shall reach this important concept of pairings by a slight extension of the Hartree-Fock method while emphasizing that the small step in methodology should not obscure the giant step in concept.

13.6.1 The reduced BCS Hamiltonian

The Hamiltonian of the fermion gas with an attractive interaction is written as

$$H = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\mathbf{k}'} V(\mathbf{k},\mathbf{k}') c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}, \tag{13.6.1}$$

where the single particle energy $\varepsilon_{\mathbf{k}}$ is measured from the Fermi energy, the spin label σ denotes the up (↑) and down (↓) spin states and the interaction is given by a simple model for ease of evaluation while retaining the essential properties,

$$V(\mathbf{k},\mathbf{k}') = -V\theta(D - |\varepsilon_{\mathbf{k}}|)\theta(D - |\varepsilon_{\mathbf{k}'}|), \tag{13.6.2}$$

with V being a positive constant. In the case of the electrons in a superconductor, the attraction may be thought of as the net result of the attractive interaction between two electrons mediated by a phonon and the direct Coulomb repulsion. The phonon is a quantized unit of energy of a crystal lattice vibration mode (see problem 16). This is a somewhat oversimplified picture. The cutoff D is then roughly of the order of the maximum phonon frequency times $\hbar$. To demonstrate the existence of the BCS state, it is sufficient to consider D much smaller than the Fermi energy. Hence, the single particle energy is $\varepsilon_{\mathbf{k}} = v_F(|\mathbf{k}| - k_F)$ to first order in the excitation vector from the Fermi surface, where $v_F = k_F/m$ is the Fermi velocity at the Fermi radius k_F. Notice that the interaction term does not contain all the terms in the general fermion-fermion interaction. The reason for keeping only the special terms containing pairs of electrons with opposite momentum and spin directions follows from the Cooper finding that the attractive interaction causes such a pair added to the Fermi sea to be unstable, i.e., having a lower energy for the whole system than the Hartree-Fock ground state, (see Problem 18).

13.6.2 The Bogoliubov-Valatin Method

The Hartree-Fock approximation may be viewed as a factorization scheme where the two particle correlation $\langle c_i^\dagger c_j^\dagger c_k c_\ell\rangle$ is approximately,

$$\langle c_i^\dagger c_j^\dagger c_k c_\ell\rangle \approx \langle c_i^\dagger c_\ell\rangle\langle c_j^\dagger c_k\rangle - \langle c_i^\dagger c_k\rangle\langle c_j^\dagger c_\ell\rangle. \tag{13.6.3}$$

The second term is the exchange counterpart of the first. Now suppose we make pairs of the four operators without regard to whether they are creation or annihilation operators, we would obtain an extra term $\langle c_i^\dagger c_j^\dagger\rangle\langle c_k c_\ell\rangle$. It may be observed that if the angular brackets denote the expectation of an N particle state, these brackets would vanish. However, to incorporate the Cooper pair, one has to use a linear combination states of different numbers of particles. Bogoliubov has shown that in the limit of infinite N the pairing states would dominate the N particle state. To proceed with the factorization scheme to include the pairing states,

$$\langle c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}\rangle \approx \langle c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger\rangle\langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}\rangle, \tag{13.6.4}$$

we actually drop the Hartree-Fock terms with the understanding that the modification of the single particle energy by the Hartree-Fock and correlation terms simply changes the Fermi velocity to $v_F = k_F/m^*$ (mass renormalization).

In the Bogoliubov-Valatin method, this is equivalent to an expansion of the pair operator

$$c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \quad = \quad \beta_k + (c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} - \beta_k), \tag{13.6.5}$$

$$\text{where} \quad \beta_k \quad = \quad \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\rangle, \tag{13.6.6}$$

is a macroscopic “condensation” of order unity and the fluctuation correction within the brackets tends to zero for large N. With the neglect of the second order fluctuation terms, the reduced Hamiltonian becomes then an effective single particle Hamiltonian,

$$H_e = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\mathbf{k}'} V(\mathbf{k},\mathbf{k}')[c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger \beta_{k'} + \beta_k^* c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} - \beta_k^*\beta_{k'}]. \tag{13.6.7}$$

The Hamiltonian may be simplified by introducing the order parameter,

$$\Delta_k = -\sum_{\mathbf{k}'} V(\mathbf{k},\mathbf{k}')\beta_{k'}, \tag{13.6.8}$$

leading to the form bilinear in the operators,

$$H_e = \sum_{\mathbf{k}} \begin{bmatrix} c^\dagger_{\mathbf{k}\uparrow} & c_{\mathbf{k}\uparrow} \end{bmatrix} \begin{bmatrix} \varepsilon_{\mathbf{k}} & -\Delta_k \\ -\Delta^*_k & -\varepsilon_{\mathbf{k}} \end{bmatrix} \begin{bmatrix} c_{\mathbf{k}\uparrow} \\ c^\dagger_{-\mathbf{k}\downarrow} \end{bmatrix} - \sum_{\mathbf{k}} (\varepsilon_{\mathbf{k}} - \Delta^*_k \beta_k). \qquad (13.6.9)$$

For the ground state, the order parameter Δ_k may be chosen to be real. The matrix is easily then diagonalized by the Bogoliubov-Valatin transformation,

$$\begin{bmatrix} c_{\mathbf{k}\uparrow} \\ c^\dagger_{-\mathbf{k}\downarrow} \end{bmatrix} = \begin{bmatrix} \cos\theta_k & \sin\theta_k \\ -\sin\theta_k & \cos\theta_k \end{bmatrix} \begin{bmatrix} \gamma_{\mathbf{k}0} \\ \gamma^\dagger_{\mathbf{k}1} \end{bmatrix}. \qquad (13.6.10)$$

The diagonalization of the 2×2 matrix in the Hamiltonian in Eq. (13.6.9) requires the value of θ_k given by

$$\tan(2\theta_k) = \frac{\Delta_k}{\varepsilon_k}. \qquad (13.6.11)$$

Thus, the eigenvalues and the state coefficients are given by

$$E_k = \sqrt{\Delta_k^2 + \varepsilon_k^2}, \qquad (13.6.12)$$

$$\cos\theta_k = \sqrt{\frac{1}{2}\left(1 + \frac{\varepsilon_k}{E_k}\right)}, \qquad (13.6.13)$$

$$\sin\theta_k = \sqrt{\frac{1}{2}\left(1 - \frac{\varepsilon_k}{E_k}\right)}. \qquad (13.6.14)$$

The transformed Hamiltonian is

$$H_e = \sum_k E_k(\gamma^\dagger_{\mathbf{k}0}\gamma_{\mathbf{k}0} + \gamma^\dagger_{\mathbf{k}1}\gamma_{\mathbf{k}1}) + \sum_k (\varepsilon_k - E_k + \Delta_k \beta_k). \qquad (13.6.15)$$

The Hamiltonian represents a system of independent fermions with energies E_k. The two new sets of one-particle states are, from the inverse of Eq. (13.6.10), defined by

$$\gamma^\dagger_{\mathbf{k}0} = c^\dagger_{\mathbf{k}\uparrow}\cos\theta_k - c_{-\mathbf{k}\downarrow}\sin\theta_k, \qquad (13.6.16)$$

$$\gamma^\dagger_{\mathbf{k}1} = c_{\mathbf{k}\uparrow}\sin\theta_k + c^\dagger_{-\mathbf{k}\downarrow}\cos\theta_k. \qquad (13.6.17)$$

The operators $\gamma^\dagger_{\mathbf{k}j}, j = 0, 1$, obey the usual anticommutation relations and each creates a fermionic quasiparticle state composed of an unusual mixture (from the Hartree-Fock viewpoint) of an electron and a hole of a time-reversed state.

The problem is a self-consistent one like the Hartree-Fock one. When the ground state is specified (see the next subsection), the occupation number of the quasi-particle state k is given by the expectation value,

$$f(E_k) = \langle \gamma^\dagger_{\mathbf{k}0} \gamma_{\mathbf{k}0} \rangle, \tag{13.6.18}$$

in terms of which the expectation value β_k defined in Eq. (13.6.6) can now be expressed:

$$\beta_k = [1 - 2f(E_k)] \sin\theta_k \cos\theta_k = [1 - 2f(E_k)] \frac{\Delta_{k'}}{2E_{k'}}. \tag{13.6.19}$$

From Eq. (13.6.8), the order parameter is then governed by the equation, known as the gap equation,

$$\Delta_k = -\sum_{k'} V(k, k')[1 - 2f(E_{k'})] \frac{\Delta_{k'}}{2E_{k'}}. \tag{13.6.20}$$

13.6.3 The BCS ground state

The ground state $|\Psi\rangle$ may be considered the vacuum states for the $\gamma^\dagger_{\mathbf{k}j}$ particles (called bogoliubons),

$$\gamma_{\mathbf{k}j} |\Psi\rangle = 0. \tag{13.6.21}$$

Thus, $f(E_k) = 0$. From the separable form of the model attractive potential in Eq. (13.6.2), the solution for the gap has the form of the step function,

$$\Delta_k = \Delta \theta(D - |\varepsilon_k|). \tag{13.6.22}$$

The solution is either $\Delta = 0$ for the normal state or for the superconducting state,

$$1 = \frac{N(0)V}{2} \int_{-D}^{D} d\varepsilon \frac{1}{\sqrt{\varepsilon^2 + \Delta^2}} = N(0)V \sinh^{-1}\left(\frac{D}{\Delta}\right), \tag{13.6.23}$$

where we have assumed that D is much less than the Fermi energy so that we may treat the density of states of the normal state Fermi gas in the range of $\pm D$ around the Fermi level to be constant at the density of states at the Fermi level, $N(0)$. Hence, the energy gap is given by

$$\Delta = \frac{D}{\sinh\left[\frac{1}{N(0)V}\right]} \approx 2D e^{-1/N(0)V}, \tag{13.6.24}$$

for small $N(0)V$.

It may be shown that the BCS variational wave function yields the ground state (Problem 20),

$$|\Psi\rangle = \prod_{v} \left(\cos\theta_k + \sin\theta_k \, c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} \right) |0\rangle, \tag{13.6.25}$$

where $|0\rangle$ is the true vacuum of no particles. The superconducting ground state energy is given by

$$E_s = \sum_k \left(\varepsilon_k - E_k + \Delta_k \beta_k \right). \tag{13.6.26}$$

The corresponding normal state energy of the system is given by letting Δ tending to zero,

$$E_n = 2 \sum_k \varepsilon_k f(\varepsilon_k). \tag{13.6.27}$$

The condensation energy which is defined as the difference between the normal state energy and the superconducting state $E_n - E_s$ is then given by

$$\begin{aligned} E_n - E_s &= 2N(0) \int_{-D}^{D} d\varepsilon \left[E - \varepsilon - \frac{\Delta^2}{E} \right], & (13.6.28) \\ &\approx \frac{1}{2} N(0) \Delta^2. & (13.6.29) \end{aligned}$$

where $E = \sqrt{\varepsilon^2 + \Delta^2}$. The final expression can be explained by the gap energy times the number of states in the gap of the order $N(0)\Delta$.

13.6.4 The excited states

To construct the excited states, we can just add bogoliubons to the ground state, such as $\gamma^{\dagger}_{\mathbf{k}j} |\Psi\rangle$. E_k is the additional energy of such a particle. The density of states of these quasi-particles per unit volume is

$$N_s(E) = \frac{1}{\Omega} \sum_k \delta(E - E_k) = N(0) \frac{E}{\sqrt{E^2 - \Delta^2}}. \tag{13.6.30}$$

Note that the number of states is conserved, i.e., there is no change from the total number of states in the normal state. The density of states can be probed by a tunnel junction made of a superconductor and a normal metal separated by a thin layer of an insulator.

13.7 Problems

1. **Normalization of boson and fermion states.**

    (a) Show that the normalization factor of $1/\sqrt{2}$ is indeed automatically generated in the two-particle state,

    $$\psi_s^\dagger(r_2)\psi_s^\dagger(r_1)|0\rangle = \frac{1}{\sqrt{2}}[|r_2\rangle_2|r_1\rangle_1 + (-1)^s|r_1\rangle_2|r_2\rangle_1], \tag{13.7.1}$$

    for bosons ($s = 0$) and fermions ($s = 1$).

    (b) The wave function of a two-particle state is $\langle r_1, r_2|\alpha, \beta\rangle$, where $\langle r_1, r_2|$ is given by the product state in Eq. (13.2.2) and the normalized state of discrete indices is given by

    $$|\alpha, \beta\rangle = C_{\alpha,\beta}c_\alpha^\dagger c_\beta^\dagger|0\rangle, \tag{13.7.2}$$

    $C_{\alpha,\beta}$ being the appropriate normalization constant you are to determine, distinguishing between the cases whether $\alpha = \beta$ or not. Find the expression of the permanent (for bosons) and determinant (for fermions) for the state wave function in terms of the single-particle wave functions $\langle r|\alpha\rangle$ and $\langle r|\beta\rangle$ in two ways:

    i. by expressing $\langle r_1, r_2|$ in the second quantized form;

    ii. by expressing $|\alpha, \beta\rangle$ as product states of $|\alpha\rangle$ and $|\beta\rangle$.

2. **A one-state system of many bosons.** Suppose that there is only one single-boson state $|\psi\rangle$ (normalized) with energy ϵ. Denote the n boson state by $|n\rangle$, where

    $$|n\rangle = |\psi\rangle_n|\psi\rangle_{n-1}\ldots|\psi\rangle_1, \tag{13.7.3}$$

    in terms of the state of each particle in its Hilbert space.

    (a) Show that in the second quantized form,

    $$|n\rangle = \frac{1}{\sqrt{n!}}(c^\dagger)^n|0\rangle, \tag{13.7.4}$$

    where $c^\dagger$ is the creation operator of the boson in state $|\psi\rangle$.

   (b) Find the Hamiltonian of the many-boson system. Show that $|n\rangle$ is its eigenstate. Find the associated eigenvalue.

   (c) Explain carefully the similarities and difference between this system and the single-particle harmonic oscillator. In particular, delineate the state $|\psi\rangle$ of the bosons and the energy eigenstates of the harmonic oscillator.

3. **A one-state fermion system.** A system of fermions has only one single-particle state $|\psi\rangle$ with energy ϵ. Denote the creation operator for a fermion in that state by $c^\dagger$.

   (a) Find the Hamiltonian in second quantized form.

   (b) Map c, $c^\dagger$, and the Hamiltonian to the Pauli spin operators σ in the spin-1/2 problem.

   (c) Are the commutation rules for the spin operators reserved?

   (d) Is it valid to assume that the Hamiltonian is isotropic in the pseudo-spin space? (Hint: does the rotation of the Hamiltonian violate the fermion number conservation?)

4. **The Hubbard model and the stability of H$^-$.** Consider the problem of putting from zero to two electrons in the hydrogen atom. Model it with four normalized states: the single proton with no electron state, $|0\rangle$; one electron in $1s$ spin-up state, $|+\rangle$; one electron in $1s$ spin-down state, $|-\rangle$; and the two-electron state in the same $1s$ singlet $|+-\rangle$.

   (a) Put the four states in the second quantized form.

   (b) Deduce the model Hamiltonian [9] including electron-electron interaction in these four basis states only in terms of the creation and annihilation operators of the $|\pm\rangle$ states in the form

$$H = \sum_\sigma \epsilon_\sigma c_\sigma^\dagger c_\sigma + u c_+^\dagger c_-^\dagger c_- c_+, \tag{13.7.5}$$

   where $\sigma = \pm$. Identify the coefficients in the Hamiltonian.

(c) Show that the four basis states given are the eigenstates of the Hamiltonian and find their eigenvalues.

(d) By comparing the eigenenergy for $|+-\rangle$ with the total energy of a neutral hydrogen atom plus an electron at infinity, show that the two-electron bound state in H$^-$ is unstable in this model. You may use the Coulomb energy evaluated in Eq. (12.3.12).

(e) The result from the model contradicts the experimental fact that two electrons do form a bound state in H$^-$. What approximate measures would you take to make a better estimate of the two-electron state?

(f) Write down the second quantized form of the perturbation term to the Hamiltonian in the presence of a circularly polarized light (left or right handed) propagating in the z direction, i.e., in the same direction as the spin-up state points.

5. **Color Quarks.** Consider a system of three quarks made of two kinds of quarks u and d. For the charge, spin and Baryon number properties, see Sec. 5.10. For the color property, see Sec. 8.6.2. Denote the state of a quark by $|q_{C,\sigma}\rangle$, where $q = u$ or d for the up and down quarks, $C = R, G, B$ for the color states, the eigenstates of λ_3 and λ_8 of the generators of SU(3), and $\sigma = \pm$ for the spin up and down states. Construct both in terms of the one-quark states and in second quantized form, the general state of

   (a) $\Delta^{++} = uuu$;

   (b) a proton, $p = uud$;

   (c) a neutron, $n = udd$.

   Explain in each case whether the color is necessary. Which state is invariant under the rotations in the color SU(3)?

6. **Anticommutation relations for fermions.** From the definition of the operators

$$\begin{aligned} \psi^\dagger(r)A_N|r_1,\ldots,r_N\rangle &= A_{N+1}|r,r_1,\ldots,r_N\rangle, \qquad (13.7.6)\\ \psi(r)A_N|r_1,\ldots,r_N\rangle &= \sum_{\ell=1}^{N}(-1)^{\ell-1}\delta(r-r_\ell)A_{N-1}|r_1,\ldots,r_{\ell-1},r_{\ell+1},\ldots,r_N\rangle, \end{aligned}$$

acting on the antisymmetrized position eigenstate $A_N|r_1,\ldots,r_N\rangle$, prove the commutation relations,

$$\begin{aligned}\{\psi(r),\psi(r')\} &= 0, && (13.7.7)\\ \{\psi(r),\psi^\dagger(r')\} &= \delta(r-r'). && (13.7.8)\end{aligned}$$

7. **Examples of Wick's theorem.** Evaluate in a non-interacting many-particle state for both the boson and fermion systems,

   (a) $\langle\Psi|\psi^\dagger(r_2)\psi^\dagger(r_1)\psi(r_1')\psi(r_2')|\Psi\rangle$;

   (b) $\langle\Psi|c_\gamma^\dagger c_\epsilon^\dagger c_\alpha c_\beta|\Psi\rangle$.

8. **Slater determinants.** Let the fermion annihilation operator be expressed in an orthonormal series

   $$\psi(r)=\sum_j\varphi_j(r)c_j. \tag{13.7.9}$$

   Show explicitly that for $N = 2,3$, the wave function $\langle r_1,\ldots,r_N|c_{j_1}^\dagger\ldots c_{j_N}^\dagger|0\rangle$ is a Slater determinant.

9. **The number-state representation.**

   Let the orthonormal set of $\{|\varphi_j\rangle\}$, $j = 0,1,2,\ldots$, be the basis set of one-particle states. An independent N-particle state can be described by the number of particles occupying each state n_j, denoted by $|n_0,n_1,\ldots,n_j,\ldots\rangle$, where $\sum_j n_j = N$. Let

   $$\psi(r)=\sum_j\varphi_j(r)c_j. \tag{13.7.10}$$

   Show that for the boson system,

   $$\begin{aligned}c_j|n_0,n_1,\ldots,n_j,\ldots\rangle &= \sqrt{n_j}|n_0,n_1,\ldots,n_j-1,\ldots\rangle,\\ c_j^\dagger|n_0,n_1,\ldots,n_j,\ldots\rangle &= \sqrt{n_j+1}|n_0,n_1,\ldots,n_j+1,\ldots\rangle; && (13.7.11)\end{aligned}$$

and for the fermion system,

$$c_j|n_0, n_1, \ldots, n_j, \ldots\rangle = (-1)^{\sum_{k=0}^{j-1} n_k} n_j |n_0, n_1, \ldots, 1-n_j, \ldots\rangle, \qquad (13.7.12)$$

$$c_k^\dagger|n_0, n_1, \ldots, n_j, \ldots\rangle = (-1)^{\sum_{k=0}^{j-1} n_k} (1-n_j) |n_0, n_1, \ldots, 1-n_j, \ldots\rangle.$$

10. **The propagator.** (Use the atomic units, i.e., $\hbar = 1$, $e' = 1$, and $m_e = 1$.) For a system of N noninteracting fermions in no external potential, the one-particle Green's function is defined as

$$G(r, t; r', t') = -i\langle T\{\psi(r,t)\psi^\dagger(r',t')\}\rangle, \qquad (13.7.13)$$

where the angular brackets denote the ground-state average,

$$\psi(r,t) = e^{iHt}\psi(r)e^{-iHt}, \qquad (13.7.14)$$

and T is the time-ordered operator,

$$T\{\psi(r,t)\psi^\dagger(r',t')\} = \begin{cases} \psi(r,t)\psi^\dagger(r',t') & \text{if } t > t'; \\ -\psi^\dagger(r',t')\psi(r,t) & \text{if } t < t'. \end{cases} \qquad (13.7.15)$$

Evaluate the Green's function by first proving that its Fourier transform is given by

$$G(k,\omega) = \frac{1-n_k}{\omega - \epsilon_k + i0} + \frac{n_k}{\omega - \epsilon_k - i0}, \qquad (13.7.16)$$

where n_k and ϵ_k are the occupation number and energy of the k state.

Express the density distribution $n(r)$, the occupation number n_k, and the total energy of the system in terms of this Green's function.

11. **The jellium.** Also known as the homogeneous electron gas. For simplicity, use the natural units in which $\hbar = 1$, $m_e = 1$, and $e^2/4\pi\epsilon_0 = 1$.

    (a) By expanding the annihilation operator in the plane-wave basis set, show that the Hamiltonian of the whole system is given by the form,

    $$H = \sum_{\mathbf{k}s} \epsilon_{ks} c_{\mathbf{k}s}^\dagger c_{\mathbf{k}s} + \frac{1}{2V} \sum_{qkk'ss'} u(q) c_{\mathbf{k}+\mathbf{q},s}^\dagger c_{\mathbf{k}'s'}^\dagger c_{\mathbf{k}'+\mathbf{q},s'} c_{\mathbf{k}s}. \qquad (13.7.17)$$

    You need to supply the meanings of the symbols.

(b) Establish the Hartree-Fock equation, find the single-electron Hartree-Fock energy and verify that indeed the single-electron eigenstate is a plane-wave state. Find the Fermi energy (the single-particle energy of the highest occupied state, i.e., at k_F).

(c) Construct the ground state in the Hartree-Fock approximation. Show that the electron occupation is given by

$$n_{ks} = \theta(k_F - k), \tag{13.7.18}$$

where the Fermi wave vector k_F is given in terms of the constant electron density n by

$$k_F^3 = 3\pi^2 n. \tag{13.7.19}$$

(d) Find the Hartree-Fock ground-state energy as the total energy per particle. (See Sec. 13.5.6).

(e) Find the kinetic and exchange parts of the chemical potential, $\mu_0(n)$ and $\mu_x(n)$ as functions of the density n.

(f) Find the single-particle "velocity" or "group velocity" as a function of k, and its behavior near k_F.

12. **Fermion pair-distribution functions.** For the system of noninteracting fermions at zero temperature:

(a) Find the spin-dependent one-particle density matrix

$$n_{mm'}(\mathbf{r}, \mathbf{r}') = \langle \Psi | \psi^\dagger(\mathbf{r}', m')\psi(\mathbf{r}, m)|\Psi\rangle, \tag{13.7.20}$$

where $m = \pm 1$ denotes the spin direction and Ψ denotes the ground state. Sketch it as a function of $|\mathbf{r} - \mathbf{r}'|$.

(b) Find the spin-dependent pair-distribution function,

$$g_{mm'}(\mathbf{r}) = \langle \Psi | \psi^\dagger(0, m')\psi^\dagger(\mathbf{r}, m)\psi(\mathbf{r}, m)\psi(0, m')|\Psi\rangle \left(\frac{2}{n}\right)^2. \tag{13.7.21}$$

Sketch it as a function of $|\mathbf{r}|$.

13. **Kohn's Theorem.**[10] A static uniform magnetic field $\mathbf{B}$ is maintained in an interacting homogeneous electron gas. Define the kinetic momentum of the whole system as

$$\mathbf{K} = \int dr \psi^\dagger(r)(\mathbf{p} + e\mathbf{A})\psi(r). \tag{13.7.22}$$

Prove that

$$\frac{d\vec{K}}{dt} = -\frac{e}{m}\mathbf{K} \times \vec{B}. \tag{13.7.23}$$

Hence, show that, if $\mathbf{B} = (0, 0, B)$ and $K_+ = K_x + iK_y$ and $|\Psi_0\rangle$ is the ground state with energy E_0, then $K_+|\Psi_0\rangle$ is an energy eigenstate of the interacting system with energy $E_0 + \hbar\omega_c$, where ω_c is the cyclotron frequency eB/m.

14. **Thomas-Fermi screening with exchange and correlation corrections.** Introduce a fixed point charge of charge e (proton charge) into a jellium of a given density n_0. Treat the potential and the change in electron density as small and the electron dynamics in the local-density approximation for the density functional terms $T_s[n]$, $E_x[n]$, and $E_c[n]$.

    (a) In the Thomas-Fermi approximation, show that the effective potential of the impurity seen by an electron is given by the form

    $$v_{\text{eff}}(r) = -\frac{e^2}{4\pi\epsilon_0 r} e^{-k_{TF} r}, \tag{13.7.24}$$

    or the Fourier transform,

    $$v_{\text{eff}}(q) \quad = \quad -\frac{e^2}{\epsilon_0(q^2 + k_{TF}^2)}. \tag{13.7.25}$$

    Supply an expression for the screening vector k_{TF}.

    (b) Find the exchange correction to the effective impurity potential.

    (c) Find the correlation correction to the effective potential. You may use any reasonable form of the correlation energy per electron.

15. **Density functional theory in the presence of a static magnetic field?**

(a) First neglect the vector potential modification of the kinetic energy (i.e. the orbital motion) and include only the spin-magnetic field term. Show explicitly how the total density $n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$ and the spin density $m(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})$ can be the two variables for the density functional of the ground-state energy. Explain how to calculate these densities.

(b) Neglect the spin part of the Hamiltonian and consider only the vector potential modification of the kinetic energy. Show by symmetry argument that the density is still a constant in a jellium if the magnetic field is uniform. Argue, therefore, that the density functional theory with only the density functional variable is not valid. Speculate what additional variables are needed.

16. **Quantization of a scalar field.** The quantization of the motion of the elastic string is perhaps the simplest example of a quantized field. We study this problem as a precursor to the quantization of the electromagnetic field.

(a) Show from first principles that the classical Hamiltonian of an elastic string is given by [14]

$$H = \int dx \left[\frac{p(x)^2}{2\rho} + \frac{\tau}{2} \left\{ \frac{\partial u(x)}{\partial x} \right\}^2 \right], \tag{13.7.26}$$

where x denotes the coordinate of a point on the string, $p(x)$ the momentum density of the string, $u(x)$ the transverse (or longitudinal) displacement of the string at x, ρ the uniform mass density of the string, and τ the uniform elastic constant in the string.

(b) To find the normal modes of vibration in classical mechanics, take the Fourier transform with box normalization with the string of length L,

$$p(x) = \frac{1}{\sqrt{L}} \sum_k p_k e^{ikx}; \tag{13.7.27}$$

$$p_k = \frac{1}{\sqrt{L}} \int dx p(x) e^{-ikx}. \tag{13.7.28}$$

The Fourier transform of $u(x)$ is defined similarly. Show that the Hamiltonian is given in terms of the normal modes as

$$H = \sum_k \left[\frac{p_k p_{-k}}{2\rho} + \frac{\tau k^2}{2} u_k u_{-k} \right]. \tag{13.7.29}$$

(c) To quantize the Hamiltonian, we note that x is just a marker for the dynamic variables $u(x)$ and $p(x)$. Thus, the commutation relation is for the material particle at x,

$$[u(x), p(x')] = i\hbar\delta(x - x'). \tag{13.7.30}$$

Define the normal mode frequency by $\omega_k = s|k|$, where $s = \sqrt{\tau/\rho}$ is the sound velocity, and, by analogy with the quantization of the harmonic oscillator, the operators,

$$a_k = \sqrt{\frac{\rho\omega_k}{2\hbar}} u_k + i\sqrt{\frac{1}{2\hbar\rho\omega_k}} p_k. \tag{13.7.31}$$

Show that the Hermitian conjugate of a_k is given by

$$a_k^\dagger = \sqrt{\frac{\rho\omega_k}{2\hbar}} u_{-k} - i\sqrt{\frac{1}{2\hbar\rho\omega_k}} p_{-k}, \tag{13.7.32}$$

and

$$[a_k, a_{k'}^\dagger] = \delta_{k,k'}. \tag{13.7.33}$$

(d) Show that

$$H = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right). \tag{13.7.34}$$

Thus, $a_k^\dagger$ creates a “phonon” of wave-vector k with energy $\hbar\omega_k$.

(e) Find the energy eigenstates and eigenvalues.

17. **The phonon propagator.** For the elastic string, the many-phonon Hamiltonian is given in the last problem. For the boson propagator, the definition is the same as Eq. (13.7.13) except that the angular brackets denote the expectation value with respect to an energy

eigenstate with phonon distribution $\{n_k\}$ and that in the time-ordering, Eq. (13.7.15) there is no change of sign when the boson operators are exchanged,

$$T\{u(r,t)u^\dagger(r',t')\} = \begin{cases} u(r,t)u^\dagger(r',t') & \text{if } t > t'; \\ u^\dagger(r',t')u(r,t) & \text{if } t < t'. \end{cases} \tag{13.7.35}$$

(a) Find the Fourier transform of the propagator $G(k,\omega)$.

(b) When the elastic string is subjected to a weak perturbation,

$$H_1 = -Fu_0(e^{ikx-i\omega t} + e^{-ikx+i\omega t}), \tag{13.7.36}$$

by evaluating the linear response function (see Chapter 10), find the Fourier transform $u(k,\omega)$ of the first order displacement $u(x,t)$ caused by the driving force.

(c) Evaluate the last part if the system is in equilibrium at temperature T.

18. **The Cooper Pair [5].**

(a) Show that, for the Hamiltonian given by Eq. (13.6.1), the state of a pair of fermions added to the Fermi sea, $\sum_k \alpha_k c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow}|\Psi_0\rangle$ with scalar coefficients α_k, satisfies the equation of the relative motion,

$$2\varepsilon_k \alpha_k + \sum_{\mathbf{k}'} V(\mathbf{k},\mathbf{k}')\alpha_{k'} = E\alpha_k, \tag{13.7.37}$$

where the pair energy E is measured from the ground state energy.

(b) Hence, show that the energy is, for the density of states at the Fermi level $N(0)$,

$$E = -2De^{-2/N(0)V}. \tag{13.7.38}$$

19. **Normal state excitations.** In analogy with the bogoliubons, the one-particle excitations of the normal Fermi sea may be expressed by letting the gap parameter tending to zero.

(a) Show that the BCS state in Eq. (13.6.25) reduces to the Fermi sea.

(b) Find the quasi-particle and quasi-hole operators for the excitation out of the Fermi sea.

(c) Sketch the one-particle excitation versus the wave vector through k_F.

20. **The BCS state.** Derive Eqs. (13.6.24), (13.6.25), (13.6.26), (13.6.29), and (13.6.30).

13.8 Source Material and Further Reading

§13.1 There is a large number of eminently readable books in the areas of manybody physics, e.g. [1, 13, 15], field theory, e.g. [22, 18, 28], and superconductivity, e.g. [21, 24].

§13.2 Second quantization is the conversion of the many-particle state to a field representation, and is, therefore, central to both many-body physics [13] and field theory [22].

§13.5 There is a great deal of literature on the density functional theory. We record here for further study the original papers on the general density functional theory [8, 10, 23, 12] and three monographs [16, 26, 6]. A somewhat dated review of the applications was given for a non-expert audience [20].

§13.6 The famous paper on the theory of superconductivity [2] can still be read today for the depth and breadth of the physics covered. Fröhlich's theory [7] predated BCS and had many of the same form but is for the pairing of the particle-hole channel. The quasiparticle theory given above follows the treatment by Bogoliubov[3] and Valatin [27]. Among the many excellent textbooks on superconductivity, two classics are [21, 24].

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[30] By making the same quotation as on p. 135 of J.M. Ziman, *Elements of Advanced Quantum Theory*, (Cambridge University Press, London, 1969), I wish to express my gratitude to my thesis supervisor.