1
Second Quantization

The physical world consists of interacting many-particle systems. An accurate description of such systems requires the inclusion of the interparticle potentials in the many-particle Schrödinger equation, and this problem forms the basic subject of the present book. In principle, the N-body wave function in configuration space contains all possible information, but a direct solution of the Schrödinger equation is impractical. It is therefore necessary to resort to other techniques, and we shall rely on second quantization, quantum-field theory, and the use of Green's functions. In a relativistic theory, the concept of second quantization is essential to describe the creation and destruction of particles.[1] Even in a nonrelativistic theory, however, second quantization greatly simplifies the discussion of many identical interacting particles.[2] This approach merely

[1] P. A. M. Dirac, *Proc. Roy. Soc. (London)*, **114A**:243 (1927).
[2] P. Jordan and O. Klein, *Z. Physik*, **45**:751 (1927); P. Jordan and E. P. Wigner, *Z. Physik*, **47**:631 (1928); V. Fock, *Z. Physik*, **75**:622 (1932). Although different in detail, the approach presented here follows the spirit of this last paper.

reformulates the original Schrödinger equation. Nevertheless, it has several distinct advantages: the second-quantized operators incorporate the statistics (Bose or Fermi) at each step, which contrasts with the more cumbersome approach of using symmetrized or antisymmetrized products of single-particle wave functions. The methods of quantum field theory also allow us to concentrate on the few matrix elements of interest, thus avoiding the need for dealing directly with the many-particle wave function and the coordinates of all the remaining particles. Finally, the Green's functions contain the most important physical information such as the ground-state energy and other thermodynamic functions, the energy and lifetime of excited states, and the linear response to external perturbations.

Unfortunately, the exact Green's functions are no easier to determine than the original wave function, and we therefore make use of perturbation theory, which is here presented in the concise and systematic language of Feynman rules and diagrams.[1] These rules allow us to evaluate physical quantities to any order in perturbation theory. We shall also show, as first observed by Feynman, that the disconnected diagrams cancel exactly. This cancellation leads to linked-cluster expansions and makes explicit the volume dependence of all physical quantities. It is possible to formulate a set of integral equations (Dyson's equations) whose iterations yield the Feynman-Dyson perturbation theory to any arbitrary order in the perturbation parameter and which are independent of the original perturbation series.[2] Since the properties of many-particle systems frequently involve expressions that are nonanalytic in the coupling constant, the possibility of nonperturbative approximations is very important.

In addition, it is frequently possible to make physical approximations that reduce the second-quantized hamiltonian to a quadratic form. The resulting problem is then exactly solvable either by making a canonical transformation or by examining the linear equations of motion.

1□THE SCHRÖDINGER EQUATION IN FIRST AND SECOND QUANTIZATION

We shall start our discussion by merely reformulating the Schrödinger equation in the language of second quantization. In almost all cases of interest, the hamiltonian takes the form

$$H = \sum_{k=1}^{N} T(x_k) + \tfrac{1}{2} \sum_{k \neq l = 1}^{N} V(x_k, x_l) \tag{1.1}$$

where T is the kinetic energy and V is the potential energy of interaction between the particles. The quantity x_k denotes the coordinates of the kth particle,

[1] R. P. Feynman, *Phys. Rev.*, **76**:749 (1949); **76**:769 (1949).
[2] F. J. Dyson, *Phys. Rev.*, **75**:486 (1949); **75**:1736 (1949).

including the spatial coordinate x_k and any discrete variables such as the z component of spin for a system of fermions or the z component of isotopic spin for a system of nucleons. The potential-energy term represents the interaction between every pair of particles, *counted once*, which accounts for the factor of $\tfrac{1}{2}$, and the double sum runs over the indices k and l separately, excluding the value k equal to l. With this hamiltonian, the time-dependent Schrödinger equation is given by

$$i\hbar \frac{\partial}{\partial t} \Psi(x_1 \cdots x_N, t) = H\Psi(x_1 \cdots x_N, t) \tag{1.2}$$

together with an appropriate set of boundary conditions for the wave function Ψ.

We start by expanding the many-particle wave function Ψ in a complete set of time-independent single-particle wave functions that incorporate the boundary conditions. For example, if we have a large homogeneous system, it is natural to expand in a set of plane waves in a large box with periodic boundary conditions; alternatively, if we have a system of interacting electrons in an atom, a complete set of single-particle coulomb wave functions is commonly used; finally, if we have particles moving in a crystal lattice, a convenient choice is the complete set of Bloch wave functions in the appropriate periodic potential. We shall use the general notation for the single-particle wave function

$$\psi_{E_k}(x_k)$$

where E_k represents a complete set of single-particle quantum numbers. For example, E_k denotes $\mathbf{p}$ for a system of spinless bosons in a box, or E, J, and M for a set of spinless particles in a central field, or $\mathbf{p}$, s_z for a homogeneous system of fermions, and so on. It is convenient to imagine that this infinite set of single-particle quantum numbers is ordered $(1, 2, 3, \ldots, r, s, t, \ldots, \infty)$ and that E_k runs over this set of eigenvalues. We can now expand the many-body wave function as follows:

$$\Psi(x_1 \cdots x_N, t) = \sum_{E_1' \cdots E_N'} C(E_1' \cdots E_N', t) \psi_{E_1'}(x_1) \cdots \psi_{E_N'}(x_N) \tag{1.3}$$

This expression is completely general and is simply the expansion of the many-particle wave function in a complete set of states. Since the $\psi_E(x)$ are time independent, all of the time dependence of the wave function appears in the coefficients $C(E_1 \cdots E_N, t)$.

Let us now insert Eq. (1.3) into the Schrödinger equation and then multiply by the expression $\psi_{E_1}(x_1)^\dagger \cdots \psi_{E_N}(x_N)^\dagger$, which is the product of the adjoint wave functions corresponding to a *fixed set of quantum numbers* $E_1 \cdots E_N$. Integrate over all the appropriate coordinates (this may include a sum over spin coordinates if the particles have spin). On the left-hand side, this procedure

projects out the coefficient C corresponding to the given set of quantum numbers $E_1 \cdots E_N$, and we therefore arrive at the equation

$$i\hbar \frac{\partial}{\partial t} C(E_1 \cdots E_N, t) = \sum_{k=1}^{N} \sum_{W} \int dx_k \, \psi_{E_k}(x_k)^\dagger \, T(x_k) \, \psi_W(x_k)$$

$$\times C(E_1 \cdots E_{k-1} \, W E_{k+1} \cdots E_N, t)$$

$$+ \tfrac{1}{2} \sum_{k \ne l = 1}^{N} \sum_{W} \sum_{W'} \iint dx_k \, dx_l \, \psi_{E_k}(x_k)^\dagger \, \psi_{E_l}(x_l)^\dagger$$

$$\times V(x_k, x_l) \, \psi_W(x_k) \, \psi_{W'}(x_l)$$

$$\times C(E_1 \cdots E_{k-1} \, W E_{k+1} \cdots E_{l-1} \, W' E_{l+1} \cdots E_N, t) \quad (1.4)$$

Since the kinetic energy is a single-particle operator involving the coordinates of the particles one at a time, it can change only one of the single-particle wave functions. The orthonormality of the single-particle wave functions ensures that all but the kth particle must have the original given quantum numbers, but the wave function of the kth particle can still run over the infinite set of quantum numbers. To be very explicit, we have denoted this variable index by W in the above equation. A similar result holds for the potential energy. The situation is a little more complicated, however, because the potential energy involves the coordinates of two particles. At most, it can change the wave functions of two particles, the kth and lth particles for example, while all the other quantum numbers must be the same as those we have projected out. The quantum numbers of the kth particle still run over an infinite set of values, denoted by W, and the quantum numbers of the lth particle still run over an infinite set of values, denoted by W'. Each given set of quantum numbers $E_1 \cdots E_N$ leads to a different equation, yielding an infinite set of coupled differential equations for the time-dependent coefficients of the many-particle wave function.

We now incorporate the statistics of the particles. The many-particle wave function is assumed to have the following property

$$\Psi(\cdots x_i \cdots x_j \cdots, t) = \pm \Psi(\cdots x_j \cdots x_i \cdots, t) \quad (1.5)$$

where, as discussed above, the coordinate x_k includes the spin for an assembly of fermions. Equation (1.5) shows that the wave function must be either symmetric or antisymmetric under the interchange of the coordinates of any two particles. A necessary and sufficient condition for Eq. (1.5) is that the expansion coefficients themselves be either symmetric or antisymmetric under the interchange of the corresponding quantum numbers

$$C(\cdots E_i \cdots E_j \cdots, t) = \pm C(\cdots E_j \cdots E_i \cdots, t) \quad (1.6)$$

The sufficiency of Eq. (1.6) is easily seen by first carrying out the particle interchange on the wave function and then carrying out the appropriate interchange

of dummy summation variables. The necessity is shown by projecting a given coefficient out of the wave function with the orthonormality of the single-particle wave functions and then using property (1.5) of the total wave function. Thus we can put all the symmetry of the wave function into the set of coefficients C.

BOSONS

Particles that require the plus sign are called *bosons*, and we temporarily concentrate on such systems. The symmetry of the coefficients under interchange of quantum numbers allows us to regroup the quantum numbers appearing in any coefficient. Out of the given set of quantum numbers $E_1 \cdots E_N$, suppose that the state 1 occurs n_1 times, the state 2 occurs n_2 times, and so on, for example,

$$C(121324 \cdots, t) = C(\underbrace{111 \cdots}_{n_1} \underbrace{222 \cdots}_{n_2} \cdots, t)$$

All of those terms in the expansion of the wave function with n_1 particles in the state 1, n_2 particles in the state 2, and so on, have the same *coefficient* in the wave function. It is convenient to give this coefficient a new name

$$\bar{C}(n_1 n_2 \cdots n_\infty, t) \equiv C(\underbrace{111 \cdots}_{n_1} \underbrace{222 \cdots}_{n_2} \cdots, t) \quad (1.7)$$

Consider the normalization of the many-particle wave function. The normalization condition can be represented symbolically as

$$\int |\Psi|^2 (d\tau) = 1 \quad (1.8)$$

which means: take the wave function, multiply it by its adjoint, and integrate over all the appropriate coordinates. The resulting normalization guarantees that the total probability of finding the system somewhere in configuration space is unity. The orthonormality of the single-particle wave functions immediately yields a corresponding condition on our expansion coefficients C

$$\sum_{E_1 \cdots E_N} |C(E_1 \cdots E_N, t)|^2 = 1 \quad (1.9)$$

We now make use of the equality of all coefficients containing the same number of particles in the same states to rewrite this condition in terms of the coefficient $\bar{C}$

$$\sum_{n_1 n_2 \cdots n_\infty} |\bar{C}(n_1 n_2 \cdots n_\infty, t)|^2 \sum_{\substack{E_1 \cdots E_N \\ (n_1 n_2 \cdots n_\infty)}} 1 = 1 \quad (1.10)$$

Here the sum is split into two pieces: first, sum over all values of the quantum numbers $E_1 E_2 \cdots E_N$ consistent with the given set of occupation numbers $(n_1 n_2 n_3 \cdots n_\infty)$, and then sum over all sets of occupation numbers. It is clear that this procedure is merely a way of regrouping all the terms in the sum. The problem of summing over all sets of quantum numbers consistent with a given set of occupation numbers is equivalent to the problem of putting

N objects into boxes with n_1 objects in the first box, n_2 objects in the second box, and so on, which can be done in $N!/n_1!n_2! \cdots n_\infty!$ ways. We thus obtain the modified normalization statement

$$\sum_{n_1 n_2 \cdots n_\infty} |\bar{C}(n_1 n_2 \cdots n_\infty, t)|^2 \frac{N!}{n_1!n_2! \cdots n_\infty!} = 1 \qquad (1.11)$$

In this relation, most of the n_i will be zero, since their total is finite

$$\sum_{i=1}^{\infty} n_i = N \qquad (1.12)$$

By definition, however, 0! is equal to 1, and Eq. (1.11) is well defined as written. Our results can be expressed more elegantly if we define still another coefficient

$$f(n_1 n_2 \cdots n_\infty, t) \equiv \left(\frac{N!}{n_1!n_2! \cdots n_\infty!}\right)^{\frac{1}{2}} \bar{C}(n_1 n_2 \cdots n_\infty, t) \qquad (1.13)$$

and the corresponding normalization statement for this set of coefficients is

$$\sum_{n_1 n_2 \cdots n_\infty} |f(n_1 n_2 \cdots n_\infty, t)|^2 = 1 \qquad (1.14)$$

where the set $\{n_i\}$ must satisfy Eq. (1.12).
The original wave function can now be rewritten as follows:

$$\Psi'(x_1 \cdots x_N, t) = \sum_{E_1 \cdots E_N} C(E_1 \cdots E_N, t) \psi_{E_1}(x_1) \cdots \psi_{E_N}(x_N)$$

$$= \sum_{E_1 \cdots E_N} \bar{C}(n_1 n_2 \cdots n_\infty, t) \psi_{E_1}(x_1) \cdots \psi_{E_N}(x_N)$$

$$= \sum_{n_1 n_2 \cdots n_\infty} f(n_1 n_2 \cdots n_\infty, t) \left(\frac{n_1!n_2! \cdots n_\infty!}{N!}\right)^{\frac{1}{2}}$$
$$\times \sum_{\substack{E_1 \cdots E_N \\ (n_1 \cdots n_\infty)}} \psi_{E_1}(x_1) \cdots \psi_{E_N}(x_N)$$

$$= \sum_{\substack{n_1 n_2 \cdots n_\infty \\ (\sum_i n_i = N)}} f(n_1 n_2 \cdots n_\infty, t)$$
$$\times \Phi_{n_1 n_2 \cdots n_\infty}(x_1 x_2 \cdots x_N) \qquad (1.15)$$

where we have defined

$$\Phi_{n_1 n_2 \cdots n_\infty}(x_1 \cdots x_N) \equiv \left(\frac{n_1!n_2! \cdots n_\infty!}{N!}\right)^{\frac{1}{2}} \sum_{\substack{E_1 \cdots E_N \\ (n_1 n_2 \cdots n_\infty)}} \psi_{E_1}(x_1) \cdots \psi_{E_N}(x_N) \qquad (1.16)$$

Equation (1.15) is an important result, and it simply says that a totally symmetric wave function can be expanded in terms of a complete orthonormal basis of completely symmetrized wave functions $\Phi_{n_1 \cdots n_\infty}(x_1 \cdots x_N)$. Furthermore,

the coefficients in this expansion are just the set of f's. Note the following properties of the Φ's

$$\Phi(\cdots x_i \cdots x_j \cdots) = \Phi(\cdots x_j \cdots x_i \cdots) \qquad (1.17)$$

$$\int dx_1 \cdots dx_N \, \Phi_{n_1' n_2' \cdots n_\infty'}(x_1 \cdots x_N)^\dagger \Phi_{n_1 n_2 \cdots n_\infty}(x_1 \cdots x_N)$$
$$= \delta_{n_1' n_1} \cdots \delta_{n_\infty' n_\infty} \qquad (1.18)$$

The first result follows immediately from interchanging particle coordinates, and then, correspondingly, dummy variables in the defining equation (1.16); the second result follows from the orthonormality of the single-particle wave functions. As an explicit example, we shall write out the wave function for three spinless bosons, two of which occupy the ground state (denoted by the subscript 1) and one of which occupies the first excited state (denoted by the subscript 2):

$$\Phi_{210\cdots0}(x_1 x_2 x_3)$$
$$= \frac{1}{\sqrt{3}} [\psi_1(1)\psi_1(2)\psi_2(3) + \psi_1(1)\psi_2(2)\psi_1(3) + \psi_2(1)\psi_1(2)\psi_1(3)]$$

We return to the analysis of Eq. (1.4), where it is important to remember that $E_1 \cdots E_N$ *is a given set of quantum numbers in this expression.* Consider first the kinetic-energy term, which can be rewritten in an obvious shorthand

$$\sum_{k=1}^{N} \sum_{W} \langle E_k|T|W\rangle C(E_1 \cdots E_{k-1} W E_{k+1} \cdots E_N, t) = \sum_{k=1}^{N} \sum_{W} \langle E_k|T|W\rangle$$
$$\times \bar{C}(n_1 n_2 \cdots n_{E_k} - 1 \cdots n_W + 1 \cdots n_\infty, t) \qquad (1.19)$$

Here, the right side makes explicit the observation that the quantum number E_k occurs one less time and the quantum number W occurs one more time. Now every time E_k takes the same value in the summation over k, let us say E (this occurs n_E times), it makes the same contribution to the sum. Therefore, and *this is the crucial point in the whole treatment,* instead of performing a sum over k from 1 to N, we can equally well sum over E and write

$$\sum_E n_E$$

That is, a sum over particles is equivalent to a sum over states, and Eq. (1.19) becomes

$$\sum_{k=1}^{N} \sum_{W} \langle E_k|T|W\rangle C(E_1 \cdots E_{k-1} W E_{k+1} \cdots E_N, t)$$
$$= \sum_E \sum_W \langle E|T|W\rangle n_E$$
$$\times \bar{C}(n_1 n_2 \cdots n_E - 1 \cdots n_W + 1 \cdots n_\infty, t) \qquad (1.20)$$

The sum on E is now infinite, running over all of the single-particle quantum numbers, but most of the n_E are zero since those states are not occupied in the original given set of quantum numbers $E_1 \cdots E_N$. Finally, it is convenient to simplify the notation, which yields

$$\sum_{k=1}^{N}\sum_{W}\langle E_k|T|W\rangle C(E_1 \cdots E_{k-1}WE_{k+1}\cdots E_N,t)=\sum_i\sum_j n_i\langle i|T|j\rangle$$
$$\times \bar{C}(n_1 n_2\cdots n_i-1\cdots n_j+1\cdots n_\infty,t)\quad (1.21)$$

Exactly the same manipulations apply to the potential energy term:

$$\frac{1}{2}\sum_{k\neq l=1}^{N}\sum_{W}\sum_{W'}\langle E_k E_l|V|WW'\rangle$$
$$\times C(E_1 \cdots E_{k-1}WE_{k+1}\cdots E_{l-1}W'E_{l+1}\cdots E_N,t)$$
$$=\frac{1}{2}\sum_{k\neq l=1}^{N}\sum_{W}\sum_{W'}\langle E_k E_l|V|WW'\rangle$$
$$\times \bar{C}(n_1 \cdots n_{E_k}-1\cdots n_W+1\cdots n_{E_l}-1\cdots$$
$$n_{W'}+1\cdots n_\infty,t)\quad(1.22)$$

As in the preceding discussion, the states E_k and E_l are each occupied one less time, and the states W and W' are each occupied one more time in this sum. Again, every time E_k takes the same value, say E (this occurs n_E times), and E_l takes the same value, say E' (this occurs $n_{E'}$ times), it makes the same contribution to the sum. There is only one slight further complication here, owing to the restriction $k\neq l$ in the double sum. Thus it is necessary to use the following counting for the number of terms appearing in this sum

$$\frac{1}{2}n_E n_{E'}\text{ if }E\neq E'\qquad \frac{1}{2}n_E(n_E-1)\text{ if }E=E'$$

because the restriction $k\neq l$ does not affect the counting if $E\neq E'$, while the eigenvalue E is counted one less time in the second sum if $E=E'$. The potential energy now becomes a doubly infinite sum, but most of the factors n_E and $n_{E'}$ are zero. Thus, just as before, we can write Eq. (1.22) as

$$\frac{1}{2}\sum_{k\neq l=1}^{N}\sum_{W}\sum_{W'}\langle E_k E_l|V|WW'\rangle$$
$$\times C(E_1 \cdots E_{k-1}WE_{k+1}\cdots E_{l-1}W'E_{l+1}\cdots E_N,t)$$
$$=\sum_E\sum_{E'}\sum_W\sum_{W'}\frac{1}{2}n_E(n_{E'}-\delta_{EE'})\langle EE'|V|WW'\rangle$$
$$\times \bar{C}(n_1 \cdots n_E-1\cdots n_W+1\cdots n_{E'}-1\cdots$$
$$n_{W'}+1\cdots n_\infty,t)$$
$$=\sum_i\sum_j\sum_k\sum_l\frac{1}{2}n_i(n_j-\delta_{ij})\langle ij|V|kl\rangle$$
$$\times \bar{C}(n_1 \cdots n_i-1\cdots n_j-1\cdots n_k+1\cdots$$
$$n_l+1\cdots n_\infty,t)\quad(1.23)$$

If the coefficients f defined in Eq. (1.13) are substituted into Eqs. (1.21) and (1.23), we arrive at the following infinite set of coupled differential equations

$$i\hbar\left[\frac{n_1!\cdots n_\infty!}{N!}\right]^{\ddagger}\frac{\partial}{\partial t}f(n_1 \cdots n_\infty,t)$$
$$=\sum_i\langle i|T|i\rangle n_i\left[\cdots\frac{n_i!\cdots}{N!}\right]^{\ddagger}f(n_1 \cdots n_i\cdots n_\infty,t)$$
$$+\sum_{i\neq j}\langle i|T|j\rangle n_i\left[\cdots\frac{(n_i-1)!\cdots(n_j+1)!\cdots}{N!}\right]^{\ddagger}$$
$$\times f(n_1 \cdots n_i-1\cdots n_j+1\cdots n_\infty,t)$$
$$+\sum_{i\neq j\neq k\neq l}\langle ij|V|kl\rangle\tfrac{1}{2}n_i n_j$$
$$\times\left[\cdots\frac{(n_i-1)!\cdots(n_j-1)!\cdots(n_k+1)!\cdots(n_l+1)!\cdots}{N!}\right]^{\ddagger}$$
$$\times f(\cdots n_i-1\cdots n_j-1\cdots n_k+1\cdots n_l+1\cdots n_\infty,t)$$
$$+\sum_{i=j\neq k\neq l}\langle ii|V|kl\rangle\tfrac{1}{2}n_i(n_i-1)$$
$$\times\left[\cdots\frac{(n_i-2)!\cdots(n_k+1)!\cdots(n_l+1)!\cdots}{N!}\right]^{\ddagger}$$
$$\times f(\cdots n_i-2\cdots n_k+1\cdots n_l+1\cdots n_\infty,t)+\text{etc.}\quad(1.24)$$

where "etc." stands for the remaining 13 possible enumerations of the equalities and inequalities between the indices i,j,k, and l. Multiplication by the factor $(N!/n_1!n_2!\cdots n_\infty!)^{\ddagger}$ on both sides of the equation finally yields the coupled set of equations

$$i\hbar\frac{\partial}{\partial t}f(n_1 \cdots n_\infty,t)=\sum_i\langle i|T|i\rangle n_i f(n_1 \cdots n_i\cdots n_\infty,t)$$
$$+\sum_{i\neq j}\langle i|T|j\rangle(n_i)^{\ddagger}(n_j+1)^{\ddagger}f(n_1 \cdots n_i-1\cdots n_j+1\cdots n_\infty,t)$$
$$+\sum_{i\neq j\neq k\neq l}\langle ij|V|kl\rangle\tfrac{1}{2}(n_i)^{\ddagger}(n_j)^{\ddagger}(n_k+1)^{\ddagger}(n_l+1)^{\ddagger}$$
$$\times f(n_1 \cdots n_i-1\cdots n_j-1\cdots n_k+1\cdots n_l+1\cdots n_\infty,t)$$
$$+\sum_{i=j\neq k\neq l}\langle ii|V|kl\rangle\tfrac{1}{2}(n_i)^{\ddagger}(n_i-1)^{\ddagger}(n_k+1)^{\ddagger}(n_l+1)^{\ddagger}$$
$$\times f(n_1 \cdots n_i-2\cdots n_k+1\cdots n_l+1\cdots n_\infty,t)+\text{etc.}\quad(1.25)$$

There is such an equation for each set of values of the occupation numbers $n_1 n_2\cdots n_\infty$; in this form, the equations are very complicated. As shown in the following discussion, however, it is possible to recast these equations in an extremely compact and elegant form.

MANY-PARTICLE HILBERT SPACE AND CREATION AND DESTRUCTION OPERATORS

We shall temporarily forget the previous analysis and instead seek a completely different quantum-mechanical basis that describes the number of particles occupying each state in a complete set of single-particle states. For this reason we introduce the *time-independent abstract state vectors*

$$|n_1 n_2 \cdots n_\infty\rangle$$

where the notation means that there are n_1 particles in the eigenstate 1, n_2 particles in the eigenstate 2, etc. We want this basis to be complete and orthonormal, which requires that these states satisfy the conditions

$$\langle n_1' n_2' \cdots n_\infty' | n_1 n_2 \cdots n_\infty \rangle$$
$$= \delta_{n_1' n_1} \delta_{n_2' n_2} \cdots \delta_{n_\infty' n_\infty} \qquad \text{orthogonality} \qquad (1.26)$$

$$\sum_{n_1 n_2 \cdots n_\infty} |n_1 n_2 \cdots n_\infty\rangle \langle n_1 n_2 \cdots n_\infty|$$
$$= 1 \qquad \text{completeness}$$

Note that the completeness sum is over all possible occupation numbers, with no restriction. To make this basis more concrete, introduce *time-independent* operators b_k, $b_k^\dagger$ that satisfy the commutation rules

$$[b_k, b_{k'}^\dagger] = \delta_{kk'} \qquad \text{bosons}$$
$$[b_k, b_{k'}] = [b_k^\dagger, b_{k'}^\dagger] = 0 \qquad (1.27)$$

These are just the commutation rules for the creation and destruction operators of the harmonic oscillator. *All of the properties* of these operators follow directly from the commutation rules, for example[1]

$$b_k^\dagger b_k |n_k\rangle = n_k |n_k\rangle \qquad n_k = 0, 1, 2, \ldots, \infty$$
$$b_k |n_k\rangle = (n_k)^{\frac{1}{2}} |n_k - 1\rangle$$
$$b_k^\dagger |n_k\rangle = (n_k + 1)^{\frac{1}{2}} |n_k + 1\rangle \qquad (1.28)$$

The number operator $b_k^\dagger b_k$ has a spectrum of eigenvalues that includes all the positive integers and zero. b_k is a destruction operator that decreases the occupation number by 1 and multiplies the state by $n_k^{\frac{1}{2}}$; $b_k^\dagger$ is a creation operator that increases the eigenvalue by one and multiplies the state by $(n_k + 1)^{\frac{1}{2}}$. The proof of these relations appears in any standard book on quantum mechanics; since it is crucial that all of these results follow directly from the commutation rules, we here include a proof of Eqs. (1.28).

[1] Compare L. I. Schiff, "Quantum Mechanics," 3d ed., pp. 182–183, McGraw-Hill Book Company, New York, 1968.

The operator $b^\dagger b$ is a hermitian operator and therefore has real eigenvalues; call this operator the *number operator*. The eigenvalues of the number operator are greater than or equal to zero, as seen from the relation

$$n = \langle n | b^\dagger b | n \rangle = \sum_m \langle n | b^\dagger | m \rangle \langle m | b | n \rangle = \sum_m |\langle m | b | n \rangle|^2 \geq 0 \qquad (1.29)$$

Now consider the commutation relation, which follows from Eq. (1.27).

$$[b^\dagger b, b] = -b \qquad (1.30)$$

With Eq. (1.30), it is easy to see that the operator b acting on an eigenstate with eigenvalue n produces a new eigenstate of the number operator but with eigenvalue reduced by one unit. This result is proved with the following relations

$$b^\dagger b(b|n\rangle) = b(b^\dagger b)|n\rangle + [b^\dagger b, b]|n\rangle$$
$$= (n - 1)(b|n\rangle) \qquad (1.31)$$

Repeated applications of b to any eigenstate must eventually give zero, since otherwise Eq. (1.31) could produce a state with a negative eigenvalue of the number operator, in contradiction to Eq. (1.29). Hence zero is one possible eigenvalue of the number operator. In exactly the same way, the adjoint commutation rule

$$[b^\dagger b, b^\dagger] = b^\dagger \qquad (1.32)$$

shows that $b^\dagger$ is the creation operator and increases the eigenvalue of the number operator by one unit. The first of Eqs. (1.28) is thus proved. Furthermore, a combination of Eqs. (1.29) and (1.31) yields the second of Eqs. (1.28), apart from an overall phase which can be chosen to be unity with no loss of generality. Finally the last of Eqs. (1.28) is proved in exactly similar fashion.[1]

The preceding discussion has been restricted to a single mode. It is, however, readily verified that the number operators for different modes commute, which means that the eigenstates of the total system can be simultaneous eigenstates of the set $\{b_k^\dagger b_k\} \equiv \{n_k\}$. In particular, our desired occupation-number basis states are simply the direct product of eigenstates of the number operator for each mode

$$|n_1 n_2 \cdots n_\infty\rangle = |n_1\rangle |n_2\rangle \cdots |n_\infty\rangle \qquad (1.33)$$

Consider now the question, can we rewrite the Schrödinger equation in terms of these more abstract state vectors? Form the following state

$$|\Psi(t)\rangle = \sum_{n_1 n_2 \cdots n_\infty} f(n_1 n_2 \cdots n_\infty, t) |n_1 n_2 \cdots n_\infty\rangle \qquad (1.34)$$

[1] If the no-particle state (or vacuum) is required to be one of our states, then the results of Eqs. (1.28) are unique.

where the f's are taken to be the set of expansion coefficients of Eq. (1.15) and satisfy the coupled partial differential equations (1.25). This state vector in the abstract Hilbert space satisfies the differential equation

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \sum_{n_1 n_2 \cdots n_\infty} i\hbar \frac{\partial}{\partial t} f(n_1 n_2 \cdots n_\infty, t)|n_1 n_2 \cdots n_\infty\rangle \qquad (1.35)$$

Since the basis state vectors are assumed to be time independent, the entire time dependence of the equation is contained in the coefficients f. As an example, look at the second kinetic-energy term in Eqs. (1.25).

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \cdots + \sum_{\substack{n_1 n_2 \cdots n_\infty \\ (\sum_1^\infty n_i = N)}} \sum_{i \neq j} \langle i|T|j\rangle f(\cdots n_i - 1 \cdots$$

$$n_j + 1 \cdots, t)(n_i)^{\frac{1}{2}}(n_j+1)^{\frac{1}{2}}|n_1 n_2 \cdots n_\infty\rangle + \cdots \qquad (1.36)$$

The dummy indices in this summation may be relabeled with the substitution

$$n_i - 1 \equiv n_i' \qquad n_j + 1 \equiv n_j' \qquad n_k \equiv n_k' \qquad (k \neq i \text{ or } j)$$

$$\sum_i n_i = \sum_i n_i' \qquad (1.37)$$

Furthermore, it is possible to sum the primed occupation numbers over exactly the same values as the original unprimed occupation numbers, because the coefficient $(n_i)^{\frac{1}{2}}(n_j + 1)^{\frac{1}{2}}$ vanishes for $n_j' = 0$ and for $n_i' = -1$. Thus Eq. (1.36) may be rewritten as

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \cdots + \sum_{\substack{n_1' n_2' \cdots n_\infty' \\ (\sum_1^\infty n_i' = N)}} \sum_{i \neq j} \langle i|T|j\rangle f(\cdots n_i' \cdots n_j' \cdots, t)$$

$$\times (n_i'+1)^{\frac{1}{2}}(n_j')^{\frac{1}{2}}|\cdots n_i'+1 \cdots n_j'-1 \cdots\rangle + \cdots \qquad (1.38)$$

Now observe that the state vector with the value of n_i' raised by one and the value n_j' lowered by one, together with the multiplicative statistical weight factor, can be simply rewritten in terms of the creation and destruction operators acting on the state vector with n_i' and n_j'

$$(n_i'+1)^{\frac{1}{2}}(n_j')^{\frac{1}{2}}|n_i' \cdots n_i'+1 \cdots n_j'-1 \cdots n_\infty'\rangle$$

$$= b_i^\dagger b_j |n_1' n_2' \cdots n_\infty'\rangle \qquad (1.39)$$

The only dependence on the occupation number left in this expression is contained in the coefficients f and in the state vector; hence the summation can be carried out and gives our original abstract state vector $|\Psi(t)\rangle$ defined by Eq. (1.34). Thus this term in the energy reduces to the following expression

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \cdots + \sum_{i \neq j} \langle i|T|j\rangle b_i^\dagger b_j |\Psi(t)\rangle + \cdots \qquad (1.40)$$

The other terms in the hamiltonian can be treated in exactly the same fashion; as a consequence, this abstract state vector $|\Psi(t)\rangle$ satisfies the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \qquad (1.41)$$

where the circumflex denotes an operator in the abstract occupation-number Hilbert space (except where this is obvious, as in the creation and destruction operators) and the hamiltonian $\hat{H}$ is given by the expression

$$\hat{H} = \sum_{ij} b_i^\dagger \langle i|T|j\rangle b_j + \tfrac{1}{2}\sum_{ijkl} b_i^\dagger b_j^\dagger \langle ij|V|kl\rangle b_l b_k \qquad (1.42)$$

It is important to distinguish between the operators and c numbers in Eq. (1.42). Thus $\hat{H}$ is an operator in this abstract occupation-number space because it depends on the creation and destruction operators. In contrast, the matrix elements of the kinetic energy and the potential energy taken between the single-particle eigenstates of the Schrödinger equation in first quantization are merely complex numbers multiplying the operators. Equations (1.41) and (1.42) together restate the Schrödinger equation in second quantization, and all of the statistics and operator properties are contained in the creation and destruction operators $b^\dagger$ and b. The physical problem is clearly unchanged by the new formulation. In particular the coefficients f specify the connection between first and second quantization.

For every solution to the original time-dependent many-particle Schrödinger equation there exists a set of expansion coefficients f. Given this set of expansion coefficients f, it is possible to construct a solution to the problem in second quantization, as shown above. Conversely, if the problem is solved in second quantization, we can determine a set of expansion coefficients f, which then yield a solution to the original time-dependent many-particle Schrödinger equation.

FERMIONS

If the negative sign in Eq. (1.6) is used, the particles are called *fermions*. The same general analysis applies, but the details are a little more complicated because of the minus signs involved in the antisymmetry of the coefficient C.

$$C(\cdots E_i \cdots E_j \cdots, t) = -C(\cdots E_j \cdots E_i \cdots, t) \qquad (1.43)$$

The C's are antisymmetric in the interchange of any two quantum numbers, which implies that the quantum number E_i must be different from the quantum number E_j or the coefficient vanishes. This result shows that the occupation number n_i must be either zero or one, which is the statement of the Pauli exclusion principle. Any coefficients that have the same states occupied are equal within a minus sign, and it is possible to define a coefficient $\bar{C}$

$$\bar{C}(n_1 n_2 \cdots n_\infty, t) = C(\cdots E_i < E_j < E_k \cdots, t) \qquad (1.44)$$

where we first arrange all the quantum numbers in the coefficient C in an increasing sequence. Exactly as before, the many-particle wave function Ψ can be expanded as

$$\Psi(x_1 \cdots x_N, t) = \sum_{n_1 \cdots n_\infty=0}^{1} f(n_1 \cdots n_\infty, t)\, \Phi_{n_1 \cdots n_\infty}(x_1 \cdots x_N) \quad (1.45)$$

where the basis wave functions Φ are given by a normalized determinant

$$\Phi_{n_1 \cdots n_\infty}(x_1 \cdots x_N) = \left(\frac{n_1! \cdots n_\infty!}{N!}\right)^{\frac{1}{2}} \begin{vmatrix} \psi_{E_1^0}(x_1) & \cdots & \psi_{E_1^0}(x_N) \\ & \vdots & \\ \psi_{E_N^0}(x_1) & \cdots & \psi_{E_N^0}(x_N) \end{vmatrix} \quad (1.46)$$

The single-particle quantum numbers of the occupied states are now assumed to be ordered $E_1^0 < E_2^0 \cdots < E_N^0$. These functions form a complete set of orthonormal antisymmetric time-independent many-particle wave functions and are usually referred to as the *Slater determinants*.[1]

It is once more convenient to introduce the abstract occupation-number space and define

$$|\Psi(t)\rangle = \sum_{n_1 n_2 \cdots n_\infty} f(n_1 n_2 \cdots n_\infty, t)|n_1 n_2 \cdots n_\infty\rangle \quad (1.47)$$

Here the coefficients f obey equations which differ from (1.25) only by phase factors [see Eq. (1.57)] and the restrictions that $n_i = 0,1$. This restriction, which reflects the particle statistics, must be incorporated into the operators in the abstract occupation-number space. As a convenient procedure, we shall follow the method of Jordan and Wigner[2] and work with *anticommutation rules*

$$\{a_r, a_s^\dagger\} = \delta_{rs} \qquad \text{fermions}$$

$$\{a_r, a_s\} = \{a_r^\dagger, a_s^\dagger\} = 0 \quad (1.48)$$

where the anticommutator is defined by the following relation

$$\{A,B\} \equiv [A,B]_+ \equiv AB + BA \quad (1.49)$$

It is easily seen that this different set of commutation rules produces the correct statistics:

1. $a_s^2 = a_s^{\dagger 2} = 0$; therefore $a_s^\dagger a_s^\dagger|0\rangle = 0$, which prevents two particles from occupying the same state.

[1] J. C. Slater, *Phys. Rev.*, **34**:1293 (1929).
[2] P. Jordan and E. P. Wigner, *loc. cit.*

2. $a^\dagger a = 1 - aa^\dagger$ (where we take the operators referring to the same mode); therefore

$$(a^\dagger a)^2 = 1 - 2aa^\dagger + aa^\dagger aa^\dagger = 1 - 2aa^\dagger + a(1 - aa^\dagger)a^\dagger = 1 - aa^\dagger = a^\dagger a \quad (1.50)$$

or

$$a^\dagger a(1 - a^\dagger a) = 0$$

This last relation implies that the number operator for the sth mode $\hat{n}_s = a_s^\dagger a_s$ has the eigenvalues zero and one, as required. Furthermore, it is straightforward to prove that the *commutator* $[\hat{n}_r, \hat{n}_s]$ vanishes, even though the individual creation and destruction operators anticommute. This result permits the simultaneous diagonalization of the set $\{\hat{n}_r\}$, in agreement with the definition of the occupation-number state vectors.

3. The anticommutation rules themselves, along with an overall choice of phase, therefore yield the following relations for the raising and lowering operators

$$a^\dagger|0\rangle = |1\rangle \qquad a|1\rangle = |0\rangle \quad (1.51)$$

$$a^\dagger|1\rangle = 0 \qquad a|0\rangle = 0$$

The anticommutation rules slightly complicate the direct-product state $|n_1 n_2 \cdots n_\infty\rangle$, because it becomes essential to keep track of *signs*. With the definition

$$|n_1 n_2 \cdots n_\infty\rangle = (a_1^\dagger)^{n_1}(a_2^\dagger)^{n_2} \cdots (a_\infty^\dagger)^{n_\infty}|0\rangle \quad (1.52)$$

we can compute directly the effect of the destruction operator a_s on this state; if $n_s = 1$, we find

$$a_s|n_1 n_2 \cdots n_\infty\rangle = (-1)^{S_s}(a_1^\dagger)^{n_1} \cdots (a_s a_s^\dagger) \cdots (a_\infty^\dagger)^{n_\infty}|0\rangle \quad (1.53)$$

where the phase factor S_s is defined by

$$S_s = n_1 + n_2 + \cdots + n_{s-1} \quad (1.54)$$

Note that if $n_s = 0$, the operator a_s can be moved all the way to the vacuum, yielding zero. If there is one particle in the state n_s, it is convenient first to use the anticommutation relation $a_s a_s^\dagger = 1 - a_s^\dagger a_s$, and then to take the a_s of the second term to the vacuum where it gives zero. Thus we finally arrive at the three relations

$$a_s|\cdots n_s \cdots\rangle = \begin{cases} (-1)^{S_s}(n_s)^{\frac{1}{2}}|\cdots n_s - 1 \cdots\rangle & \text{if } n_s = 1 \\ 0 & \text{otherwise} \end{cases}$$

$$a_s^\dagger|\cdots n_s \cdots\rangle = \begin{cases} (-1)^{S_s}(n_s + 1)^{\frac{1}{2}}|\cdots n_s + 1 \cdots\rangle & \text{if } n_s = 0 \\ 0 & \text{otherwise} \end{cases} \quad (1.55)$$

$$a_s^\dagger a_s|\cdots n_s \cdots\rangle = n_s|\cdots n_s \cdots\rangle \qquad n_s = 0,1$$

The third relation is the most useful, for it shows that the number operator introduces no extra phases. The reason for writing the first two equations with the factor $(n_s)^{\frac{1}{2}}$ and $(n_s+1)^{\frac{1}{2}}$ instead of the more familiar notation using n_s and $1-n_s$ is that they now assume *exactly the same form as before, or vanish, except for the extra phase factor* $(-1)^{S_s}$.

As an example of the role played by this factor in the case of fermions, consider the kinetic-energy term in Eq. (1.4)

$$i\hbar\frac{\partial}{\partial t}C(E_1\cdots E_N,t)=\sum_{k=1}^{N}\sum_{W}\langle E_k|T|W\rangle$$
$$\times C(E_1\cdots E_{k-1}WE_{k+1}\cdots E_N,t)+\cdots \quad (1.56)$$

where $E_1\cdots E_N$ is a given set of quantum numbers. These quantum numbers can be reordered simultaneously on *both sides of this equation* into the proper sequence. One problem remains, however, because the quantum number W appears on the right, where E_k appears on the left. If W is moved to its proper place in the ordered form, an extra phase factor

$$(-1)^{n_W+n_{W+2}+\cdots+n_{E_k}-1}\quad W<E_k$$
$$(-1)^{n_{E_k+1}+n_{E_k+2}+\cdots+n_{W}-1}\quad W>E_k \quad (1.57)$$

is needed, representing the number of interchanges to put W in its proper place. Just as before, we now go over to the f coefficients and again change variables. For example, consider part of the kinetic-energy term

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle=\cdots+\sum_{n_1'n_2'\cdots n_\infty'}\sum_{i<j}\langle i|T|j\rangle$$
$$\times f(\cdots n_i'\cdots n_j'\cdots,t)(n_i'+1)^{\frac{1}{2}}(n_j')^{\frac{1}{2}}\delta_{n_i'0}\delta_{n_j'1}$$
$$\times(-1)^{n_{i+1}'+n_{i+2}'+\cdots+n_{j-1}'}|\cdots n_i'+1\cdots n_j'-1\cdots\rangle+\cdots \quad (1.58)$$

Note that the phase factor appearing in this expression is equivalent to $(-1)^{S_j-S_i-n_i'}$; furthermore, this term contributes only if n_i' is equal to 0 and n_j' is equal to 1, so that this phase factor is just $(-1)^{S_j-S_i}$. Equations (1.55) now allow us to rewrite the relevant factor as

$$\delta_{n_i'0}\delta_{n_j'1}(n_i'+1)^{\frac{1}{2}}(n_j')^{\frac{1}{2}}(-1)^{S_j-S_i}|\cdots n_i'+1\cdots n_j'-1\cdots\rangle$$
$$=a_i^\dagger a_j|n_i'\cdots n_\infty'\rangle \quad (1.59)$$

which demonstrates that the creation and destruction operators *defined with the anticommutation rules* indeed have the required properties. In this way the Schrödinger equation again assumes the following form in second quantization

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle=\hat{H}|\Psi(t)\rangle$$
$$\hat{H}=\sum_{rs}a_r^\dagger\langle r|T|s\rangle a_s+\frac{1}{2}\sum_{rstu}a_r^\dagger a_s^\dagger\langle rs|V|tu\rangle a_u a_t \quad (1.60)$$

Note particularly the ordering of the final two destruction operators in the hamiltonian, which is opposite that of the last two single-particle wave functions in the matrix elements of the potential (the reader is urged to verify this in detail for himself). In the case of bosons, of course, this ordering is irrelevant because the final two destruction operators commute with each other, but for fermions the order affects the overall sign. Exactly as before, Eq. (1.60) is wholly equivalent to the Schrödinger equation in first quantization, but the phases arising from the antisymmetry of the expansion coefficients have been incorporated into the hamiltonian and the direct-product state vectors.

2□FIELDS

It is often convenient to form the linear combinations of the creation and destruction operators (denoted $c^\dagger$ and c for generality)

$$\hat{\psi}(\mathbf{x})\equiv\sum_k\psi_k(\mathbf{x})c_k$$
$$\hat{\psi}^\dagger(\mathbf{x})\equiv\sum_k\psi_k(\mathbf{x})^\dagger c_k^\dagger \quad (2.1)$$

where the coefficients are the single-particle wave functions and the sum is over the complete set of single-particle quantum numbers. In particular, the index k for spin-$\frac{1}{2}$ fermions may denote the set of quantum numbers $\{\mathbf{k},s_z\}$ or $\{E,L,J,M\}$ and the corresponding wave functions have two components

$$\psi_k(\mathbf{x})=\begin{bmatrix}\psi_k(\mathbf{x})_1\\\psi_k(\mathbf{x})_2\end{bmatrix}\equiv\psi_k(\mathbf{x})_\alpha\quad \alpha=1,2 \quad (2.2)$$

These quantities $\hat{\psi}$ and $\hat{\psi}^\dagger$ are called *field operators*. They are operators in this abstract occupation-number Hilbert space because they depend on the creation and destruction operators. The field operators satisfy simple commutation or anticommutation relations depending on the statistics

$$[\hat{\psi}_\alpha(\mathbf{x}),\hat{\psi}_\beta^\dagger(\mathbf{x}')]_\mp=\sum_k\psi_k(\mathbf{x})_\alpha\,\psi_k(\mathbf{x}')_\beta^*=\delta_{\alpha\beta}\delta(\mathbf{x}-\mathbf{x}') \quad (2.3a)$$
$$[\hat{\psi}_\alpha(\mathbf{x}),\hat{\psi}_\beta(\mathbf{x}')]_\mp=[\hat{\psi}_\alpha^\dagger(\mathbf{x}),\hat{\psi}_\beta^\dagger(\mathbf{x}')]_\mp=0 \quad (2.3b)$$

where the upper (lower) sign refers to bosons (fermions). Here the first equality in Eq. (2.3a) follows from the commutation or anticommutation relations for the creation and destruction operators, and the second follows from the completeness of the single-particle wave functions.

The hamiltonian operator can be rewritten in terms of these field operators as follows:

$$\hat{H}=\int d^3x\,\hat{\psi}^\dagger(\mathbf{x})T(\mathbf{x})\hat{\psi}(\mathbf{x})+\frac{1}{2}\iint d^3x\,d^3x'\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')V(\mathbf{x},\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}) \quad (2.4)$$

This expression is readily verified since the integration over spatial coordinates produces the single-particle matrix elements of the kinetic energy and potential

space separates into a sequence of problems in the subspaces corresponding to a fixed total number of particles. Nevertheless, *the abstract Hilbert space contains states with any number of particles.*

3□EXAMPLE: DEGENERATE ELECTRON GAS

To illustrate the utility of second quantization, we consider a simple model that provides a first approximation to a metal or a plasma. This system is an interacting electron gas placed in a uniformly distributed positive background chosen to ensure that the total system is neutral. In a real metal or plasma, of course, the positive charge is localized in the ionic cores, whose dynamical motion must also be included in the calculation. These positive ions are much heavier than the electrons, however, and it is permissible to neglect the ionic motion entirely. In contrast, the assumption of a uniform background is more drastic; for this reason, the present model can provide only a qualitative account of real metals.

We are interested in the properties of the bulk medium. It therefore is convenient to enclose the system in a large cubical box with sides of length L; the limit $L \to \infty$ will be taken at the end of the calculation. In a uniform infinite medium, all physical properties must be invariant under spatial translation; this observation suggests the use of periodic boundary conditions on the single-particle wave functions, which then become plane-wave states

$$\psi_{k\lambda}(\mathbf{x}) = V^{-\frac{1}{2}} e^{i\mathbf{k}\cdot\mathbf{x}} \eta_\lambda \qquad (3.1)$$

Here $V(\equiv L^3)$ is the volume of the box, and η_λ are the two spin functions for spin-up and spin-down along a chosen z axis,

$$\eta_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \eta_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \qquad (3.2)$$

The periodic boundary conditions determine the allowed wavenumbers as

$$k_i = \frac{2\pi n_i}{L} \qquad i = x, y, z \qquad n_i = 0, \pm1, \pm2, \ldots$$

The total hamiltonian can be written as the sum of three terms

$$H = H_{el} + H_b + H_{el-b} \qquad (3.3)$$

where

$$H_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} e^2 \sum_{i \neq j}^{N} \frac{e^{-\mu|\mathbf{r}_i - \mathbf{r}_j|}}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad (3.4)$$

is the hamiltonian for the electrons,

$$H_b = \tfrac{1}{2} e^2 \iint d^3x \, d^3x' \frac{n(\mathbf{x}) n(\mathbf{x}') e^{-\mu|\mathbf{x} - \mathbf{x}'|}}{|\mathbf{x} - \mathbf{x}'|} \qquad (3.5)$$

energy, leaving a sum of these matrix elements multiplied by the appropriate creation and destruction operators. An additional matrix element in spin space is implied if the particles have spin-½. Note carefully the ordering of the last two field operators in the potential energy, which agrees with our previous remarks and ensures that $\hat{H}$ is hermitian. In this form, the hamiltonian suggests the name *second quantization*, for the above expression looks like the expectation value of the hamiltonian taken between wave functions. The quantities $\hat{\psi}$ and $\hat{\psi}^\dagger$ are not wave functions, however, but field operators; thus in second quantization the fields are the operators and the potential and kinetic energy are just complex coefficients.

The extension to any other operator is now clear from the foregoing analysis. For example, consider a general one-body operator

$$J = \sum_{i=1}^{N} J(\mathbf{x}_i) \qquad (2.5)$$

written in first-quantized form. The corresponding second-quantized operator is given by

$$\hat{J} = \sum_{rs} \langle r|J|s\rangle c_r^\dagger c_s$$
$$= \int d^3x \sum_{rs} \psi_r(\mathbf{x})^\dagger J(\mathbf{x}) \psi_s(\mathbf{x}) c_r^\dagger c_s$$
$$= \int d^3x \, \hat{\psi}^\dagger(\mathbf{x}) J(\mathbf{x}) \hat{\psi}(\mathbf{x}) \qquad (2.6)$$

where the last form is especially useful. In particular, the number-density operator

$$n(\mathbf{x}) = \sum_{i=1}^{N} \delta(\mathbf{x} - \mathbf{x}_i) \qquad (2.7)$$

becomes

$$\hat{n}(\mathbf{x}) = \sum_{rs} \psi_r(\mathbf{x})^\dagger \psi_s(\mathbf{x}) c_r^\dagger c_s = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \qquad (2.8)$$

while the total-number operator assumes the simple form

$$\hat{N} = \int d^3x \, \hat{n}(\mathbf{x}) = \sum_r c_r^\dagger c_r = \sum_r \hat{n}_r$$
$$= \int d^3x \, \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \qquad (2.9)$$

because of the orthonormality of the single-particle wave functions. The number operator commutes with the hamiltonian of Eq. (2.4), as can be verified by using either the commutation rules for the creation and destruction operators or those of the field operators. This result is physically obvious since the ordinary Schrödinger hamiltonian does not change the total number of particles. We infer that $\hat{N}$ is a constant of the motion and can be diagonalized simultaneously with the hamiltonian. Thus the problem in the abstract Hilbert

is the energy of the positive background whose particle density is $n(\mathbf{x})$, and

$$H_{el-b} = -e^2 \sum_{i=1}^{N} \int d^3x \, \frac{n(\mathbf{x}) \, e^{-\mu|\mathbf{x}-\mathbf{r}_i|}}{|\mathbf{x}-\mathbf{r}_i|}$$ (3.6)

is the interaction energy between the electrons and the positive background. We have inserted an exponential convergence factor to define the integrals, and μ will eventually be allowed to vanish. Because of the long-range nature of the coulomb interaction, the three terms in Eq. (3.3) individually diverge in the "thermodynamic limit" $N \to \infty$, $V \to \infty$, but $n = N/V$ constant. The entire system is neutral, however, and the sum of these terms must remain meaningful in this limit. The presence of the convergence factor μ ensures that the expressions are mathematically well defined at every step and allows us to make this cancellation explicit. Since we are interested in the bulk properties of the neutral medium, for example E/N (which depends only on n), our limiting procedure will be first $L \to \infty$ and then $\mu \to 0$. Equivalently, we can assume $\mu^{-1} \ll L$ at each step in our calculation; this allows us to shift the origin of integration at will, apart from surface corrections, which are negligible in this limit.

In Eq. (3.3) the only dynamical variables are those referring to the electrons, because the positive background is inert. Thus H_b is a pure c number and is readily evaluated for a uniform distribution $n(\mathbf{x}) = N/V$:

$$H_b = \tfrac{1}{2}e^2 \left(\frac{N}{V}\right)^2 \iint \int d^3x \, d^3x' \frac{e^{-\mu|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|}$$
$$= \tfrac{1}{2}e^2 \left(\frac{N}{V}\right)^2 \int \int d^3x \int d^3z \, \frac{e^{-\mu z}}{z}$$
$$= \tfrac{1}{2}e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$ (3.7)

Here the translational invariance has been used to shift the origin of integration in the second line. The quantity $N^{-1}H_b$ diverges in the limit $\mu \to 0$, because the long range of the coulomb potential allows every element of charge to interact with every other one.

In principle, H_{el-b} is a one-particle operator since it acts on each electron. For the present system, however, we may again use the translational invariance to write

$$H_{el-b} = -e^2 \sum_{i=1}^{N} \frac{N}{V} \int d^3x \, \frac{e^{-\mu|\mathbf{x}-\mathbf{r}_i|}}{|\mathbf{x}-\mathbf{r}_i|}$$
$$= -e^2 \sum_{i=1}^{N} \frac{N}{V} \int d^3z \, \frac{e^{-\mu z}}{z}$$
$$= -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$ (3.8)

showing that H_{el-b} is in fact a c number. The total hamiltonian thus reduces to

$$H = -\tfrac{1}{2}e^2 N^2 V^{-1} 4\pi\mu^{-2} + H_{el}$$ (3.9)

and all of the interesting physical effects are contained in H_{el}. We shall now rewrite Eq. (3.9) in second quantization. The kinetic-energy term requires the matrix element

$$\langle \mathbf{k}_1 \lambda_1 | T | \mathbf{k}_2 \lambda_2 \rangle = (2mV)^{-1} \int d^3x \, e^{-i\mathbf{k}_1 \cdot \mathbf{x}} \eta_{\lambda_1}^{\dagger} (-\hbar^2 \nabla^2) e^{i\mathbf{k}_2 \cdot \mathbf{x}} \eta_{\lambda_2}$$
$$= \frac{\hbar^2 k_2^2}{2mV} \delta_{\lambda_1 \lambda_2} \int d^3x \, e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{x}}$$
$$= \frac{\hbar^2 k_2^2}{2m} \delta_{\lambda_1 \lambda_2} \delta_{\mathbf{k}_1 \mathbf{k}_2}$$ (3.10)

where the usual definition of the Kronecker delta

$$\int d^3x \, e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{x}} = V \delta_{\mathbf{k}_1 \mathbf{k}_2}$$ (3.11)

has been used. The kinetic-energy operator becomes

$$\hat{T} = \sum_{\mathbf{k}\lambda} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda}$$ (3.12)

which can be interpreted as the kinetic energy of each mode multiplied by the corresponding number operator. For the potential energy it is necessary to evaluate the following more complicated matrix element

$$\langle \mathbf{k}_1 \lambda_1 \mathbf{k}_2 \lambda_2 | V | \mathbf{k}_3 \lambda_3 \mathbf{k}_4 \lambda_4 \rangle = \frac{e^2}{V^2} \iint \int d^3x_1 \, d^3x_2 \, e^{-i\mathbf{k}_1 \cdot \mathbf{x}_1} \eta_{\lambda_1}(1)^{\dagger}$$
$$\times e^{-i\mathbf{k}_2 \cdot \mathbf{x}_2} \eta_{\lambda_2}(2)^{\dagger} \frac{e^{-\mu|\mathbf{x}_1 - \mathbf{x}_2|}}{|\mathbf{x}_1 - \mathbf{x}_2|}$$
$$\times e^{i\mathbf{k}_3 \cdot \mathbf{x}_1} \eta_{\lambda_3}(1) \, e^{i\mathbf{k}_4 \cdot \mathbf{x}_2} \eta_{\lambda_4}(2)$$ (3.13)

With the substitution $\mathbf{x} = \mathbf{x}_2$ and $\mathbf{y} = \mathbf{x}_1 - \mathbf{x}_2$, this expression reduces to

$$\langle \mathbf{k}_1 \lambda_1 \mathbf{k}_2 \lambda_2 | V | \mathbf{k}_3 \lambda_3 \mathbf{k}_4 \lambda_4 \rangle = \frac{e^2}{V^2} \int d^3x \, e^{-i(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \cdot \mathbf{x}}$$
$$\times \int d^3y \, e^{i(\mathbf{k}_3 - \mathbf{k}_1) \cdot \mathbf{y}} \frac{e^{-\mu y}}{y} \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4}$$
$$= \frac{e^2}{V} \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \delta_{\mathbf{k}_1 + \mathbf{k}_2, \, \mathbf{k}_3 + \mathbf{k}_4} \frac{4\pi}{(\mathbf{k}_1 - \mathbf{k}_3)^2 + \mu^2}$$ (3.14)

where the Kronecker deltas in the spin indices arise from the orthogonality of the spin wave functions. Once again, we have shifted the origin of integration, and

the final Kronecker delta represents the conservation of momentum in a uniform system. The total hamiltonian can now be written as

$$\hat{H} = -\frac{1}{2}\frac{e^2 N^2}{V}\frac{4\pi}{\mu^2} + \sum_{\mathbf{k}\lambda}\frac{\hbar^2 k^2}{2m}a^\dagger_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda} + \frac{e^2}{2V}$$
$$\times \sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}\sum_{\mathbf{k}_3\lambda_3}\sum_{\mathbf{k}_4\lambda_4}\delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4}\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{k}_3+\mathbf{k}_4}$$
$$\times \frac{4\pi}{(\mathbf{k}_1-\mathbf{k}_3)^2 + \mu^2}a^\dagger_{\mathbf{k}_1\lambda_1}a^\dagger_{\mathbf{k}_2\lambda_2}a_{\mathbf{k}_4\lambda_4}a_{\mathbf{k}_3\lambda_3} \qquad (3.15)$$

The electrical neutrality of our system makes it possible to eliminate μ from the hamiltonian, as we shall now show. The conservation of momentum really limits the summation over $\{\mathbf{k}_i\}$ to three independent variables instead of four. The change of variables

$$\mathbf{k}_1 = \mathbf{k}+\mathbf{q} \qquad \mathbf{k}_3 = \mathbf{k}$$
$$\mathbf{k}_2 = \mathbf{p}-\mathbf{q} \qquad \mathbf{k}_4 = \mathbf{p}$$

guarantees that $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{k}_4$, and furthermore identifies $\hbar(\mathbf{k}_1 - \mathbf{k}_3) = \hbar\mathbf{q}$ as the momentum transferred in the two-particle interaction. With these new variables, the last term of Eq. (3.15) becomes

$$\frac{e^2}{2V}\sum_{\mathbf{k}\mathbf{p}\mathbf{q}}\sum_{\lambda_1\lambda_2}\frac{4\pi}{q^2+\mu^2}a^\dagger_{\mathbf{k}+\mathbf{q},\lambda_1}a^\dagger_{\mathbf{p}-\mathbf{q},\lambda_2}a_{\mathbf{p}\lambda_2}a_{\mathbf{k}\lambda_1} \qquad (3.16)$$

where two of the spin summations have been evaluated with the Kronecker deltas. It is convenient to separate Eq. (3.16) into two terms, referring to $\mathbf{q} \neq 0$ and $\mathbf{q} = 0$, respectively,

$$\frac{e^2}{2V}\sum_{\mathbf{k}\mathbf{p}\mathbf{q}}{}'\sum_{\lambda_1\lambda_2}\frac{4\pi}{q^2+\mu^2}a^\dagger_{\mathbf{k}+\mathbf{q},\lambda_1}a^\dagger_{\mathbf{p}-\mathbf{q},\lambda_2}a_{\mathbf{p}\lambda_2}a_{\mathbf{k}\lambda_1}$$
$$+\frac{e^2}{2V}\sum_{\mathbf{k}\mathbf{p}}\sum_{\lambda_1\lambda_2}\frac{4\pi}{\mu^2}a^\dagger_{\mathbf{k}\lambda_1}a^\dagger_{\mathbf{p}\lambda_2}a_{\mathbf{p}\lambda_2}a_{\mathbf{k}\lambda_1} \qquad (3.17)$$

where the prime on the first summation means: omit the term $\mathbf{q} = 0$. The second summation may be rewritten with the anticommutation relation as

$$\frac{e^2}{2V}\frac{4\pi}{\mu^2}\sum_{\mathbf{k}\lambda_1}\sum_{\mathbf{p}\lambda_2}a^\dagger_{\mathbf{k}\lambda_1}a_{\mathbf{k}\lambda_1}(a^\dagger_{\mathbf{p}\lambda_2}a_{\mathbf{p}\lambda_2}-\delta_{\mathbf{k}\mathbf{p}}\delta_{\lambda_1\lambda_2}) = \frac{e^2}{2V}\frac{4\pi}{\mu^2}(\hat{N}^2 - \hat{N})$$

where Eq. (2.9) has been used to identify $\hat{N}$. Since we shall always deal with states of fixed N, the operator $\hat{N}$ may be replaced by its eigenvalue N, thereby yielding a c-number contribution to the hamiltonian

$$\frac{e^2 N^2}{2V}\frac{4\pi}{\mu^2}-\frac{e^2 N}{2V}\frac{4\pi}{\mu^2} \qquad (3.18)$$

It is clear that the first term of Eq. (3.18) cancels the first term of Eq. (3.15). The second term of Eq. (3.18) represents an energy $-\frac{1}{4}\pi e^2(V\mu^2)^{-1}$ per particle and vanishes in the proper physical limit discussed previously: first $L \to \infty$ and then $\mu \to 0$ (always keeping $\mu^{-1} \ll L$). Thus the explicit μ^{-2} divergence cancels identically in the thermodynamic limit, which reflects the electrical neutrality of the total system; furthermore, it is now permissible to set $\mu = 0$ in the first term of Eq. (3.17), since the resulting expression is well defined. We therefore obtain the final hamiltonian for a bulk electron gas in a uniform positive background

$$\hat{H} = \sum_{\mathbf{k}\lambda}\frac{\hbar^2 k^2}{2m}a^\dagger_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda} + \frac{e^2}{2V}\sum_{\mathbf{k}\mathbf{p}\mathbf{q}}{}'\sum_{\lambda_1\lambda_2}\frac{4\pi}{q^2}a^\dagger_{\mathbf{k}+\mathbf{q},\lambda_1}a^\dagger_{\mathbf{p}-\mathbf{q},\lambda_2}a_{\mathbf{p}\lambda_2}a_{\mathbf{k}\lambda_1} \qquad (3.19)$$

where it is understood that the limit $N \to \infty$, $V \to \infty$, $N/V = n$ = constant is implicitly assumed.

It is now convenient to introduce dimensionless variables. We define a length r_0 in terms of the volume per particle:

$$V \equiv \frac{4}{3}\pi r_0^3 N \qquad (3.20)$$

r_0 is essentially the interparticle spacing. The coulomb interaction provides a second length, given by the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2} \qquad (3.21)$$

and the (dimensionless) ratio between these two quantities

$$r_s \equiv \frac{r_0}{a_0} \qquad (3.22)$$

evidently characterizes the density of the system. With r_0 as the unit of length, we define the following quantities

$$\bar{V} = r_0^{-3}V \qquad \bar{\mathbf{k}} = r_0\mathbf{k} \qquad \bar{\mathbf{p}} = r_0\mathbf{p} \qquad \bar{\mathbf{q}} = r_0\mathbf{q} \qquad (3.23)$$

and thus obtain the following dimensionless form of Eq. (3.19)

$$\hat{H} = \frac{e^2}{a_0 r_s^2}\left(\sum_{\bar{\mathbf{k}}\lambda}\frac{1}{2}\bar{k}^2 a^\dagger_{\bar{\mathbf{k}}\lambda}a_{\bar{\mathbf{k}}\lambda} + \frac{r_s}{2\bar{V}}\sum_{\bar{\mathbf{k}}\bar{\mathbf{p}}\bar{\mathbf{q}}}{}'\sum_{\lambda_1\lambda_2}\frac{4\pi}{\bar{q}^2}a^\dagger_{\bar{\mathbf{k}}+\bar{\mathbf{q}},\lambda_1}a^\dagger_{\bar{\mathbf{p}}-\bar{\mathbf{q}},\lambda_2}a_{\bar{\mathbf{p}}\lambda_2}a_{\bar{\mathbf{k}}\lambda_1}\right) \qquad (3.24)$$

This is an important result, for it shows that the potential energy becomes a small perturbation as $r_s \to 0$, corresponding to the high-density limit ($r_0 \to 0$). Thus the leading term in the interaction energy of a high-density electron gas can be obtained with first-order perturbation theory, even though the potential is neither weak nor short range. One might expect that the ground-state energy has a power-series expansion in the small parameter r_s, but, in fact, the second-

order term diverges logarithmically (see Probs. 1.4 and 1.5). Instead, the series takes the form

$$E = \frac{Ne^2}{a_0 r_s^2}(a + b r_s + c r_s^2 \ln r_s + d r_s^3 + \cdots)$$

where $a, b, c, d \cdots$ are numerical constants. We shall now evaluate a and b, while c may be inferred from the calculation in Prob. 1.5. The proper calculation of c and higher coefficients is very difficult, however, and requires the more elaborate techniques developed in Chaps. 3 to 5.

In the high-density limit, the preceding discussion enables us to separate the original dimensional form of the hamiltonian [Eq. (3.19)] into two parts:

$$\hat{H}_0 = \sum_{k\lambda} \frac{\hbar^2 k^2}{2m} a_{k\lambda}^\dagger a_{k\lambda}$$ (3.25a)

$$\hat{H}_1 = \frac{e^2}{2V} {\sum_{kpq}}' \sum_{\lambda_1 \lambda_2} \frac{4\pi}{q^2} a_{k+q,\lambda_1}^\dagger a_{p-q,\lambda_2}^\dagger a_{p\lambda_2} a_{k\lambda_1}$$ (3.25b)

where $\hat{H}_0$ is the unperturbed hamiltonian, representing a noninteracting Fermi system, and $\hat{H}_1$ is the (small) perturbation. Correspondingly, the ground-state energy E may be written as $E^{(0)} + E^{(1)} + \cdots$, where $E^{(0)}$ is the ground-state energy of a free Fermi gas, while $E^{(1)}$ is the first-order energy shift. Since the Pauli exclusion principle allows only two fermions in each momentum eigenstate, one with spin-up and one with spin-down, the normalized ground-state $|F\rangle$ is obtained by filling the momentum states up to a maximum value, the Fermi momentum $p_F = \hbar k_F$. In the limit that the volume of the system becomes infinite, we can replace sums over states by integrals with the following familiar relation

$$\sum_{k\lambda} f_\lambda(\mathbf{k}) = \sum_{n_x n_y n_z} \sum_\lambda f_\lambda\left(\frac{2\pi n}{L}\right) \xrightarrow[L\to\infty]{} \iiint dn_x\, dn_y\, dn_z \sum_\lambda f_\lambda\left(\frac{2\pi n}{L}\right)$$
$$= V(2\pi)^{-3} \sum_\lambda \int d^3k\, f_\lambda(\mathbf{k})$$ (3.26)

Here, Eq. (3.2) has been used to convert the sum over momenta into a sum over the integers characterizing the wavenumbers. For very large L, the function f varies slowly when the integers change by unity so that n_x, n_y, and n_z may be considered continuous variables. Finally, Eq. (3.2) again allows us to replace the variables $\{n_i\}$ by $\{k_i\}$, leaving an integral over wavenumbers.

The maximum wavenumber k_F is determined by computing the expectation value of the number operator in the ground state $|F\rangle$

$$N = \langle F|\hat{N}|F\rangle = \sum_{k\lambda}\langle F|\hat{n}_{k\lambda}|F\rangle = \sum_{k\lambda}\theta(k_F - k)$$
$$= V(2\pi)^{-3}\sum_\lambda \int d^3k\, \theta(k_F - k) = (3\pi^2)^{-1} V k_F^3 = N$$ (3.27)

where $\theta(x)$ denotes the step function

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases}$$ (3.28)

This important relation between the Fermi wavenumber k_F and the particle density $n \equiv N/V$ will be used repeatedly in subsequent work; an alternative form

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac13} = \left(\frac{9\pi}{4}\right)^{\frac13} r_0^{-1} \approx 1.92 r_0^{-1}$$ (3.29)

shows that k_F^{-1} is comparable with the interparticle spacing. The expectation value of $\hat{H}_0$ may be evaluated in the same fashion

$$E^{(0)} = \langle F|\hat{H}_0|F\rangle = \frac{\hbar^2}{2m}\sum_{k\lambda} k^2\langle F|\hat{n}_{k\lambda}|F\rangle$$
$$= \frac{\hbar^2}{2m}\sum_{k\lambda} k^2\theta(k_F - k)$$
$$= \frac{\hbar^2}{2m}\sum_\lambda V(2\pi)^{-3}\int d^3k\, k^2\theta(k_F - k)$$ (3.30)
$$= \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} N = \frac{e^2}{2a_0}\frac{N}{r_s^2}\frac{3}{5}\left(\frac{9\pi}{4}\right)^{\frac13} = \frac{e^2}{2a_0}N\frac{2.21}{r_s^2}$$

In a free Fermi gas, the ground-state energy per particle $E^{(0)}/N$ is $\frac35$ of the Fermi energy $\epsilon_F^0 = \hbar^2 k_F^2/2m$; alternatively $E^{(0)}/N$ may be expressed as $2.21 r_s^{-2}$ ry(rydberg), where 1 ry $= e^2/2a_0 \approx 13.6$ eV is the ground-state binding energy of a hydrogen atom.

We shall now compute the first-order energy shift

$$E^{(1)} = \langle F|\hat{H}_1|F\rangle$$
$$= \frac{e^2}{2V}{\sum_{kpq}}'\sum_{\lambda_1\lambda_2}\frac{4\pi}{q^2}\langle F|a_{k+q,\lambda_1}^\dagger a_{p-q,\lambda_2}^\dagger a_{p\lambda_2} a_{k\lambda_1}|F\rangle$$ (3.31)

The matrix element is readily analyzed as follows: the states $p\lambda_2$ and $k\lambda_1$ must be occupied in the ground state $|F\rangle$, since the destruction operators acting to the right would otherwise give zero. Similarly the states $\mathbf{k} + \mathbf{q}, \lambda_1$ and $\mathbf{p} - \mathbf{q}, \lambda_2$ must also be occupied in $|F\rangle$, since the operators $a^\dagger$ acting to the left would otherwise give zero. Finally, the same state appears on each side of the matrix element, which requires the two creation operators to fill up the holes made by the two destruction operators. The operators must therefore be paired off, and there are only two possibilities:

$$\mathbf{k} + \mathbf{q}, \lambda_1 = \mathbf{k}\lambda_1 \qquad\qquad \mathbf{k} + \mathbf{q}, \lambda_1 = \mathbf{p}\lambda_2$$
$$\text{or}$$
$$\mathbf{p} - \mathbf{q}, \lambda_2 = \mathbf{p}\lambda_2 \qquad\qquad \mathbf{p} - \mathbf{q}, \lambda_2 = \mathbf{k}\lambda_1$$ (3.32)

The first pairing is here forbidden because the term $\mathbf{q} = 0$ is excluded from the sum, and the matrix element becomes

$$\delta_{\mathbf{k}+\mathbf{q},\mathbf{p}}\,\delta_{\lambda_1\lambda_2}\langle F|a^\dagger_{\mathbf{k}+\mathbf{q},\lambda_1}\,a^\dagger_{\mathbf{k}\lambda_1}\,a_{\mathbf{k}+\mathbf{q},\lambda_1}\,a_{\mathbf{k}\lambda_1}|F\rangle$$

$$= -\delta_{\mathbf{k}+\mathbf{q},\mathbf{p}}\,\delta_{\lambda_1\lambda_2}\langle F|\hat{n}_{\mathbf{k}+\mathbf{q},\lambda_1}\,\hat{n}_{\mathbf{k}\lambda_1}|F\rangle$$

$$= -\delta_{\mathbf{k}+\mathbf{q},\mathbf{p}}\,\delta_{\lambda_1\lambda_2}\,\theta(k_F - |\mathbf{k}+\mathbf{q}|)\,\theta(k_F - k) \quad (3.33)$$

A combination of Eqs. (3.31) and (3.33) yields

$$E^{(1)} = -\frac{e^2}{2V}\sum_{\lambda_1}\sum_{\mathbf{kq}}{}'\frac{4\pi}{q^2}\,\theta(k_F - |\mathbf{k}+\mathbf{q}|)\,\theta(k_F - k)$$

$$= -\frac{e^2}{2}\frac{4\pi V}{(2\pi)^6}\,2\int d^3k\,d^3q\,q^{-2}\,\theta(k_F - |\mathbf{k}+\mathbf{q}|)\,\theta(k_F - k) \quad (3.34)$$

where the factor 2 arises from the spin sum, and the restriction $\mathbf{q} \neq 0$ may now be omitted since it affects the integrand at only a single point. It is convenient to change variables from $\mathbf{k}$ to $\mathbf{P} = \mathbf{k} + \tfrac{1}{2}\mathbf{q}$, which reduces Eq. (3.34) to the symmetrical form

$$E^{(1)} = -4\pi e^2\,V(2\pi)^{-6}\int d^3q\,q^{-2}\int d^3P\,\theta(k_F - |\mathbf{P}+\tfrac{1}{2}\mathbf{q}|)\,\theta(k_F - |\mathbf{P}-\tfrac{1}{2}\mathbf{q}|)$$

The region of integration over $\mathbf{P}$ is shown in Fig. 3.1. Both particles lie inside the Fermi sea, so that $|\mathbf{P}+\tfrac{1}{2}\mathbf{q}|$ and $|\mathbf{P}-\tfrac{1}{2}\mathbf{q}|$ must both be smaller than k_F.

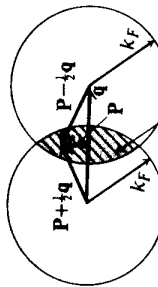Region $\begin{cases}|\mathbf{P}+\tfrac{1}{2}\mathbf{q}|<k_F\\ |\mathbf{P}-\tfrac{1}{2}\mathbf{q}|<k_F\end{cases}$ **Fig. 3.1** Integration region in momentum space for $E^{(1)}$.

The evaluation of this volume is a simple problem in geometry, with the result

$$\int d^3P\,\theta(k_F - |\mathbf{P}+\tfrac{1}{2}\mathbf{q}|)\,\theta(k_F - |\mathbf{P}-\tfrac{1}{2}\mathbf{q}|) = \frac{4\pi}{3}k_F^3(1 - \tfrac{3}{2}x + \tfrac{1}{2}x^3)\,\theta(1 - x)$$

$$x \equiv \frac{q}{2k_F} \quad (3.35)$$

The remaining calculation is elementary, and we find

$$E^{(1)} = -4\pi e^2\,V(2\pi)^{-6}\frac{4}{3}\pi k_F^3\,2k_F\int_0^1 dx\,4\pi(1 - \tfrac{3}{2}x + \tfrac{1}{2}x^3)$$

$$= \frac{e^2}{2a_0}\frac{N}{r_s}\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{3}{2\pi} = -\frac{e^2}{2a_0}N\frac{0.916}{r_s} \quad (3.36)$$

Thus the ground-state energy per particle in the high-density limit is given approximately as

$$\frac{E}{N}\bigg|_{r_s\to 0} = \frac{e^2}{2a_0}\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \cdots\right] \quad (3.37)$$

Note that the energy per particle is finite, which shows that the total energy is an extensive quantity. The first term in Eq. (3.37) is simply the kinetic energy of the Fermi gas of electrons; it becomes the dominant term as $r_s \to 0$, that is, in the limit of very high densities. The second term is known as the *exchange energy* and is negative. It arises because the evaluation of the matrix element in Eq. (3.31) involves two terms [Eq. (3.32)], direct and exchange, owing to the antisymmetry of the wave functions. As we have seen, the direct term arises from the $\mathbf{q} = 0$ part of the interaction and serves to cancel $H_b + H_{el-b}$. This
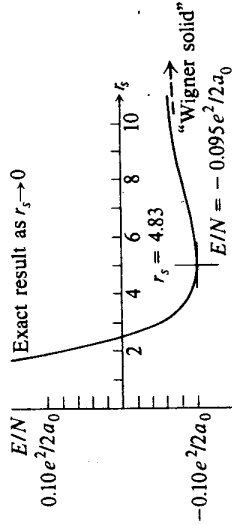

Fig. 3.2 Approximate ground-state energy [first two terms in Eq. (3.37)] of an electron gas in a uniform positive background.

cancellation leads to the restriction $\mathbf{q} \neq 0$ and reflects the electrical neutrality of the system. All that remains is the (negative) exchange energy. The remaining terms in this series (indicated by dots) are called the *correlation energy*;[1] we shall return to this problem in Secs. 12 and 30, where the leading term in the correlation energy will be evaluated explicitly.

For the present, however, it is interesting to consider the first two terms of Eq. (3.37) as a function of r_s (Fig. 3.2). The attractive sign of the exchange energy ensures that the curve has a minimum occurring for negative values of the energy; the system is therefore bound. As $r_s \to 0$ (the high-density limit), Eq. (3.37) represents the exact solution to the problem. For larger values of r_s, our solution is only approximate, but we can now use the familiar Rayleigh-Ritz variational principle, which asserts that the *exact* ground state of a quantum-mechanical system always has a lower energy than that evaluated by taking the expectation value of the total hamiltonian in any normalized state. The conditions of this principle are clearly satisfied, since we have merely computed the expectation value of the hamiltonian $\hat{H}$ in the state $|F\rangle$. It follows that the

[1] E. P. Wigner, *Phys. Rev.*, 46:1002 (1934).

the energy per particle in this solid is given asymptotically by

$$\frac{E}{N}\bigg|_{r_s\to\infty} = \frac{e^2}{2a_0}\left[-\frac{1.79}{r_s} + \frac{2.66}{r_s^{3/2}} + \cdots\right] \qquad \text{"Wigner solid"} \qquad (3.43)$$

and it is clear that this expression gives a lower value of the energy than that of Eq. (3.37). The low-density limit [Eq. (3.43)] is sketched as the dotted line in Fig. 3.2. The variational principle guarantees that this Wigner solid represents a better wave function as $r_s \to \infty$, because it has a lower energy.

PROBLEMS

1.1. Prove that the number operator $\hat{N} = \int \psi^\dagger(\mathbf{x})\psi(\mathbf{x})d^3x$ commutes with the hamiltonians of Eqs. (1.42) and (1.60).

1.2. Given a homogeneous system of spin-½ particles interacting through a potential V
(a) show that the expectation value of the hamiltonian in the noninteracting ground state is

$$E^{(0)} + E^{(1)} = 2\sum_{\mathbf{k}}^{k_F}\frac{\hbar^2\mathbf{k}^2}{2m} + \frac{1}{2}\sum_{\mathbf{k}\lambda}^{k_F}\sum_{\mathbf{k}'\lambda'}^{k_F}\{\langle\mathbf{k}\lambda\mathbf{k}'\lambda'|V|\mathbf{k}\lambda\mathbf{k}'\lambda'\rangle$$
$$-\langle\mathbf{k}\lambda\mathbf{k}'\lambda'|V|\mathbf{k}'\lambda'\mathbf{k}\lambda\rangle\}$$

where λ is the z component of the spin.
(b) Assume V is central and spin independent. If $V(|\mathbf{x}_1 - \mathbf{x}_2|) < 0$ for all $|\mathbf{x}_1 - \mathbf{x}_2|$ and $\int|V(x)|d^3x < \infty$, prove that the system will collapse (*Hint*: start from $(E^{(0)} + E^{(1)})/N$ as a function of density).

1.3. Given a homogeneous system of spin-zero particles interacting through a potential V
(a) show that the expectation value of the hamiltonian in the noninteracting ground state is $E^{(1)}/N = (N-1)V(0)/2V \approx \frac{1}{2}nV(0)$, where

$$V(\mathbf{q}) = \int d^3x\, V(\mathbf{x})e^{-i\mathbf{q}\cdot\mathbf{x}} \qquad \text{and} \qquad V(0) \text{ means } V(\mathbf{q}=0)$$

(b) Repeat Prob. 1.2b.
(c)‡ Show that the second-order contribution to the ground-state energy is

$$\frac{E^{(2)}}{N} = -\frac{N-1}{2V}\int\frac{d^3q}{(2\pi)^3}\frac{|V(\mathbf{q})|^2}{\hbar^2\mathbf{q}^2/m} \approx -\frac{n}{2}\int\frac{d^3q}{(2\pi)^3}\frac{|V(\mathbf{q})|^2}{\hbar^2\mathbf{q}^2/m}$$

‡ Use standard second-order perturbation theory: If $H = H_0 + H_1$, and the unperturbed eigenvectors $|j\rangle$ satisfy $H_0|j\rangle = E_j|j\rangle$, then

$$E^{(2)} = \sum_{j\neq 0}\frac{|\langle 0|H_1|j\rangle|^2}{E_0 - E_j} = \langle 0|H_1\frac{P}{E_0 - H_0}H_1|0\rangle$$

where $|0\rangle$ is the ground-state eigenvector of H_0 with energy E_0, and $P = 1 - |0\rangle\langle 0|$ is a projection operator on the excited states.

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exact solution to our model problem must also represent a bound system with energy lying below the curve in Fig. 3.2. The minimum of Eq. (3.37) occurs at the values

$$(r_s)_{min} = 4.83 \qquad \left(\frac{E}{N}\right)_{min} = -0.095\,\frac{e^2}{2a_0} \qquad (3.38)$$

Although there is no reason to expect that our solution is correct in this region, it is interesting to observe that these values

$$r_s = 4.83 \qquad \frac{E}{N} = -1.29 \text{ eV} \qquad \text{at minimum} \qquad (3.39)$$

compare favorably with the experimental values for metallic sodium under laboratory conditions[1]

$$r_s = 3.96 \qquad \frac{E}{N} = -1.13 \text{ eV} \qquad \text{Na (experiment)} \qquad (3.40)$$

where the binding energy is the heat of vaporization of the metal. Thus this very simple model is able to explain the largest part of the binding energy of metals. In real metals, one must further localize the positive background of charge on the crystal lattice sites, as first discussed by Wigner and Seitz.[2,3]

It is also interesting to use Eq. (3.37) to evaluate the thermodynamic properties of the electron gas. The pressure is given by

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = -\frac{dE}{dr_s}\frac{dr_s}{dV} = \frac{Ne^2}{2a_0}\frac{r_s}{3V}\left[\frac{2(2.21)}{r_s^3} - \frac{0.916}{r_s^2}\right] \qquad (3.41)$$

The pressure vanishes at the point $r_s = 4.83$, where the system is in equilibrium. Furthermore, the bulk modulus

$$B = -V\left(\frac{\partial P}{\partial V}\right)_N = \frac{Ne^2}{2a_0}\frac{2}{9V}\left[\frac{5(2.21)}{r_s^3} - \frac{2(0.916)}{r_s^2}\right] \qquad (3.42)$$

vanishes at the higher value $r_s = 6.03$, where the system ceases to be metastable in this approximation.

In the low-density limit ($r_s \to \infty$) Wigner[4] has shown that one can obtain a lower energy of the system by allowing the electrons to "crystallize" in a "Wigner solid." This situation occurs because the zero-point kinetic energy associated with localizing the electrons eventually becomes negligible in comparison to the electrostatic energy of a classical lattice. Wigner has shown that

[1] See, for example, C. Kittel, "Quantum Theory of Solids," p. 115, John Wiley and Sons, Inc., New York, 1963.
[2] E. P. Wigner and F. Seitz, *Phys. Rev.*, **43**:804 (1933); **46**:509 (1934).
[3] A modern account of the relevant corrections may be found in C. Kittel, *op. cit.*, pp. 93–94, 115.
[4] E. P. Wigner, *Trans. Farad. Soc.*, **34**:678 (1938); W. J. Carr, Jr., *Phys. Rev.*, **122**:1437 (1961).