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Quantum Condensates: An Overview

Anthony J. Leggett
Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois

1. Introduction

As we all know, single microscopic particles such as electrons or atoms do not behave according to the familiar classical (Newtonian) physics which describes the everyday world, but rather according to the prescriptions of quantum mechanics, the outcome is often bizarre and counterintuitive. When a macroscopic number of such particles (say $\sim 10^{23}$) is assembled under conditions where the effects of quantum mechanics are important, the results can be even more spectacular; they include *macroscopic* phenomena such as superfluidity and superconductivity, which are completely impossible to explain in classical terms. Most, though not all[1] of these exotic phenomena, are a result of a phenomenon which I shall refer to generically as "quantum condensation," in which a macroscopic number of particles or pairs of particles—a nonzero fraction of all particles present—occupy a single quantum state; this phenomenon is traditionally referred to as Bose-Einstein condensation (BEC) when it occurs in a system of bosons such as liquid ^{4}He, and as Cooper pairing when it occurs, for pairs of particles, in a system of fermions such as the electrons in a superconducting metal. As a result of quantum condensation, the characteristically quantum-mechanical behavior which we are used to seeing at the level of single electrons is as it were amplified by the cooperation of condensed particles and can manifest itself at the macroscopic level.

The present essay is intended as a general introduction to the subject of quantum condensation and its consequences, as manifested in a variety of physical systems. I will try to review the fundamental physical ideas, usually without detailed derivation[2], and compare the theoretical predictions with the observed experimental behavior of the relevant systems. I will confine myself to phenomena observable under terrestrial ("laboratory") conditions, and so will not explicitly address the question of quantum condensation as it may occur, for example, in neutron stars.

2. When are quantum effects important?

In discussing the circumstances under which many-particle systems can show nonclassical and possibly exotic behavior, it is essential to distinguish between two kinds of effects, which for clarity, I shall call respectively those of quantum *mechanics* and those of quantum *statistics*. By the effects of quantum *mechanics*, I simply mean the result of replacing the Newtonian description of particle dynamics by one based on the Schrödinger equation. Such effects of course show up already at the single-particle level; a typical example of their manifestation in a many-body system would be the fact that the low-temperature specific heat C_v of an insulating crystalline solid is not given by the classical equipartition theorem but rather by the Debye law $C_v \propto T^3$. While such effects are often quantitatively very important in macroscopic systems, they do not usually, by themselves, give rise to particularly exotic forms of behavior.

By the effects of quantum *statistics*, I mean something more, namely the consequences of the characteristic *indistinguishability*, in the quantum description, of elementary particles of the same type. As is well known, elementary particles can be separated into two classes according to the value of their intrinsic angular momentum ("spin") in

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[1] A well-known example of a macroscopic state which is not directly related to the phenomenon of quantum condensation, but nevertheless has very exotic properties, is the fractional quantum Hall effect.

[2] Most of the ideas I will discuss here are treated in considerably greater detail in my recent book ([4]) which in particular provides derivations of many statements made below without proof. I refer to this book throughout as QL.

units of Dirac's constant $\hbar$: those with spin $n\hbar$, where n is any integer including zero ("bosons"), and those with spin $n\hbar/2$ where n is an *odd* integer ("fermions"). Electrons, neutrons and protons have spin 1/2 and are thus fermions: photons have spin 1 and so are bosons.

It is a fundamental consequence[3] of the indistinguishability of elementary particles that the many-body Schrödinger wave function must be either symmetric or antisymmetric under exchange of identical particles. That is, if $\boldsymbol{r}_1$ and σ_1 denote, respectively, the coordinates and the spin projection on some arbitrarily chosen axis of particle 1, and $\boldsymbol{r}_2$ and σ_2 the corresponding variables for particle 2, then if 1 and 2 are of identical nature we must have

$$\Psi(\boldsymbol{r}_1\sigma_1 : \boldsymbol{r}_2\sigma_2) = \pm\, \Psi(\boldsymbol{r}_2\sigma_2 : \boldsymbol{r}_1\sigma_1) \qquad (1)$$

The celebrated *spin-statistics theorem*, the proof of which requires the apparatus of relativistic quantum field theory (see e.g. [7]), assures us that the + sign applies in the case of bosons and the − sign for fermions. An immediate consequence of eqn. (1) for fermions is the *Pauli principle*: no two identical fermions can be in the same state (have identical quantum numbers). These considerations are formalized in the so-called second-quantization notation, but for our purposes the simple Schrödinger description with the constraint (1) will be adequate.

The considerations of the last paragraph apply as they stand only to "elementary" particles such as electrons and protons. What about composite objects such as the ^4He atom (composed of 2 protons, 2 neutrons and 2 electrons)? For a reason to be discussed in the next paragraph, the only symmetry we need worry about in this case is that corresponding to the only process[4] for which there is any appreciable probability amplitude, namely exchange of two atoms as wholes. If the atom in question contains a total of N_F fermions, then the factor required by eqn. (1) is $(-1)^{N_F}$. Thus, for example, the neutral atoms ^4He ($N_F = 6$) and $^{87}Rb(N_F = 124)$ behave as bosons, while $^3He(N_F = 5)$ and $^{40}K(N_F = 59)$ are fermions. As we will see below, liquids of the isotopes ^3He and ^4He, despite being identical in their chemical properties and differing only modestly in mass, behave in spectacularly different ways; this is a dramatic illustration of the importance of the difference in "statistics."

It is very important to appreciate that the (anti) symmetrization constraint (1) only has physical significance to the extent that the identical particles in question can change places; otherwise they have, as it were, no means of "knowing" that they are identical. A nice illustration of this principle is a comparison of the vibrational and rotational levels of homoatomic diatomic molecules such as C_2 for the case of homonuclear (e.g. $^{12}C_2$) and heteronuclear (e.g. $^{12}C -^{14} C$) molecules; the vibrational levels (which do not involve the atoms changing places) are identical[5] in the two cases, while in the rotational spectrum (which does involve) all values of relative angular momentum K occur for the heteronuclear case, but for the homonuclear case, in accordance with (1), only even values occur.[6] (Note that in the case of the rotational motion it is not required that the two identical atoms are ever at the same point in space at the same time; it is enough that (when viewed classically) they change places.) The above general principle explains why, in the case of complex objects such as the ^4He atom, we do not need to concern ourselves explicitly with the symmetry under, e.g., exchange of a single neutron between the two nuclei with the other nucleons and electrons held fixed; such processes have essentially zero amplitude to occur under conditions of experimental interest.

Assembling the above considerations, we can now determine the conditions which must be satisfied if a system of particles of a given type is to show not only the effects of quantum mechanics but also those of quantum statistics. A rough-and-ready criterion for the effects of quantum *mechanics* not to be swamped by thermal motion is that the thermal energy k_BT should be $\lesssim$ the characteristic spacing of the energy levels of the system. For a dense system of particles it is reasonable to assume that the characteristic spread of the groundstate wave function, Δx, should be of the order of $n^{-1/3}$ whose n is the particle density. Then by the uncertainty principle, the momentum uncertainty Δp is

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[3] In 3 or more spatial dimensions. In 2D(and 1D) there are additional exotic possibilities ("anyons"), see [5].

[4] Exchange of single fermions typically requires tunnelling through a large distance and is exponentially suppressed. Cf. below.

[5] Apart from a trivial effect coming from the difference in the reduced mass in the two cases.

[6] Even (odd) values of K correspond to a relative wave function even (odd) under exchange of the two atoms.

$\sim \hbar n^{1/3}$, and we may estimate the spacing of the energy levels as $\sim (\Delta p)^2/2m$, where m is the mass of the particle in question. Thus the condition for the effects of quantum mechanics (the Schrödinger description) to be appreciable is

$$k_B T \lesssim n^{2/3}\hbar^2/m \tag{2}$$

Condition (2) (which actually turns out to be somewhat on the pessimistic side) is certainly fulfilled for any system of electrons and even atoms at typical solid or liquid density at temperatures which are nowadays routinely attainable in the laboratory.

However, as already pointed out, if in addition to the effects of quantum mechanics we wish to see those of quantum *statistics*, then it is necessary to ensure, in addition, that particles in question have a reasonable probability amplitude to change places. In a typical solid, either crystalline or amorphous, such amplitudes (for the atoms) are usually exceedingly small; and the same holds for the electrons if the solid in question is an insulator. On the other hand, in an ordinary gas it is impossible to fulfill condition (2)[7], since the vapor pressure (i.e. n) tends to zero much faster than T. Consequently, with one proviso to be discussed below, any system which is to show appreciable effects of quantum statistics must be in some sense or other in the *liquid* phase, and for this reason such systems are often called "quantum liquids." The major known examples of terrestrial quantum liquids are: (1) the two stable isotopes of helium (^3He and ^4He) in the liquid phase; (2) the electrons in a typical metal; (3) ultracold trapped atomic gases, typically of alkali atoms. The last case, of course, does not fit the conventional definition of a "liquid" (in fact, typical densities are a factor $\sim 10^{-3}$ of that of air at STP!); it is able to fulfill condition (2) only because recombination of the atoms to form molecules and eventually the (generally stable) solid phase is strongly inhibited by various rather stringent conservation rules, so that the gas phase is stable over sufficiently long times ($\sim$ secs-mins) for experiments to be possible on it.

Although there exist "quantum liquid" phases which do not show the phenomenon of quantum condensation (for example, those of the electrons in a nonsuperconducting metal, or of liquid ^3He above $3mK$), and these are of considerable interest in their own right, I will not discuss them in this essay. Rather, I will proceed right away to that class of quantum liquids, namely the quantum-condensed ones, which show the most spectacular quantum effects at the macroscopic scale.

3. Quantum condensation

The very simplest example of a many-body system exhibiting the phenomenon of quantum condensation is a free gas of spinless particles obeying Bose statistics in three dimensions.[8] If we enclose such a system in a cubic box of side L with periodic boundary conditions, then the single-particle energy eigenstates are plane waves with wave vector $\boldsymbol{k}$ such that $k_i = 2\pi\ell_i/L (i = x, y, z)$ with the ℓ_i integral (note that the "zero-momentum" ($\boldsymbol{k} = 0$) state $\ell_x = \ell_y = \ell_z = 0$ is allowed), and with energy $\mathcal{E}_k = \hbar^2 k^2/2m$ (so that the energy of the $\boldsymbol{k} = 0$ state is zero). Because of the requirement (1) (with the + sign) on the many-body wave function, there is *one and only one* state of the many-body system which corresponds to having exactly n_1 particles in single-particle states 1, n_2 in state 2, etc. What this means, intuitively, is that the "entropic" factor $N!/\prod_i n_i!$ which, in a system not subject to the constraint(1) would tend to favor a wide distribution of particles over the available single-particle states, is removed, and thus many-body states with a large concentration of particles in a single one-particle state are no longer entropically disfavored as they would be in that case. More quantitatively, a standard statistical-mechanical argument (see e.g. [3, section 53] shows that when the system is held at (a sufficiently high) temperature T the average number of particles in the single-particle state $\boldsymbol{k}$ is given by the Bose distribution

$$\langle n_k\rangle(T,\mu) = \left(\exp\beta(\mathcal{E}_k - \mu) - 1\right)^{-1} \quad (\beta \equiv 1/k_B T) \tag{3}$$

In formula (3) the quantity μ is the chemical potential, which must be fixed by the requirement that the *average* value of the total number of particles as calculated from (3) should be equal to the total number N which we actually have in the system,

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[7] We did not actually show that for a dilute phase such as a gas, condition (2) is necessary. However, we will see below that this is in fact so.

[8] While no existing experimental system exactly implements this idealized model, a dilute gas of ^4He atoms in the metastable ^3S state ($^4He^*$), with spins strongly aligned by a magnetic field, comes close to it.

i.e. that

$$\sum_k \langle n_k \rangle (T, \mu) = N \tag{4}$$

Note that for (3) to make sense we must have $\mu \leq 0$.

Now it is easy to show from (3) and (4) that in the limit $T \to \infty$ the quantity μ tends to $-\infty$ (so that we recover the classical Maxwell-Boltzmann distribution). But since the sum on the LHS of (4) is an increasing function of both μ and T, it is clear that decreasing temperature leads to an increase of μ, and moreover (given that $\mu \leq 0$) that an upper bound on the LHS of (4) is its value for the given T and $\mu = 0$. So, if it should turn out that this value is less than N, we are in trouble! Will this actually happen? Well, since we intend as usual to take the thermodynamic limit ($V \to \infty, N \to \infty,\ N/V \to \text{const}$), and in this limit the allowed values of k and hence of $\mathcal{E}_k$ are very closely spaced, it is tempting when evaluating the LHS of eqn. (4) to make the standard approximation of replacing the sum by an integral. If we do that, then we find that the quantity $\sum_k \langle n_k (T, \mu = 0) \rangle$ as thus evaluated is equal to $N(T/T_c)^{3/2}$, where the "critical temperature" T_c is given by the expression

$$k_B T_c = 3 \cdot 31 \, n^{2/3} \, \hbar^2 / m \tag{5}$$

Note that this temperature is exactly of the order of magnitude of the temperature below which we estimated, according to eqn. (2), that quantum effects would be significant (the latter is sometimes called the "degeneracy temperature"); an order-of-magnitude estimate of T_c (though not, of course, its exact numerical value) may be obtained by simply setting the number of single-particle states with energy less than the thermal energy $k_B T$ equal to the total particle number N.

What happens in the case of $T \leq T_c$ when eqn. (4), as evaluated in the above approximation, can no longer be fulfilled? This question was examined by Einstein in a famous 1925 paper, with the conclusion that under these conditions a nonzero fraction of all the particles, that is a macroscopic number N_o, occupy a *single* one-particle state, namely that with $\boldsymbol{k} = 0$ and thus zero energy. The remaining particles occupy the $\boldsymbol{k} \neq 0$ states, and their contribution to the LHS of (4) may be legitimately calculated, as above, by replacing the sum by an integral and is equal to $N(T/T_c)^{3/2}$. Thus we obtain for the "condensate fraction" $N_o(T)/N$ the result

$$\frac{N_0(T)}{N} = 1 - (T/T_c)^{3/2} \quad \text{(free Bose gas)} \tag{6}$$

This macroscopic occupation of a single one-particle state is known as *Bose-Einstein condensation* (BEC)[9]; it, or rather its generalization to more realistic systems, is at the root of the spectacular macroscopic phenomena displayed by quantum liquids.

Let's now consider the more realistic case of a system of interacting Bose particles, such as ^4He atoms; for the moment let us imagine that they are in thermal equilibrium in zero external potential (e.g. in a box of volume V with periodic boundary conditions, so that the zero-momentum state ($\boldsymbol{k} = 0$) is still available). Although the quantity n_k is no longer a good quantum number, it is still possible to ask about its expectation value $\langle n_k(T) \rangle$ (where the $\langle \ \ \rangle$ now denote not only thermal but quantum-mechanical averaging), and in particular to ask whether the quantity $\langle n_o(T) \rangle$ (hereafter denoted $N_o(T)$) is a nonzero fraction of the total particle number N in the thermodynamic limit, i.e. whether BEC occurs. It is clear that the answer cannot be an unqualified yes, since we know from experiment that at pressures above ~ 26 atoms a system of ^4He atoms forms a regular crystalline solid, and it is easy to show that such a solid has $N_o(T) \sim 0(1)$ in the thermodynamic limit. However, in a theoretical *tour de force* more than 40 years ago, Gavoret and Nozières showed that *provided* the groundstate can be obtained from that of the noninteracting Bose gas by applying perturbation theory in the inter-atomic interaction, N_o/N is indeed of order 1 in the thermodynamic limit. In fact, it is almost universally believed that this is the case in liquid ^4He; however, the $T = 0$ "condensate fraction" $N_o(0)/N$, which can be estimated from neutron scattering data, is not 100% as it would be for a free Bose gas but closer to 10%. It is also almost universally believed that the so-called lambda-transition of liquid ^4He , which occurs at a temperature (T_λ) of $2 \cdot 17K$ (at saturated vapor pressure) marks the onset of BEC in the liquid; this hypothesis is consistent with the fact that for a free Bose gas of the mass and density of ^4He the value of T_c predicted from eqn. (5) would

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[9] The above argument for BEC (which is the standard textbook one) might reasonably be questioned, on the grounds that to introduce the chemical potential and thus obtain eqn. (3) we had to relax the constraint of particle number conservation, whereas we appear to have invoked it in eqn. (4). For a derivation which avoids this difficulty, see [6].

be about $3K$. The so-called He-II phase which occurs below the lambda-transition has many very anomalous properties including superfluidity, and as we shall see below that, this is to be expected if it is indeed characterized by the presence of BEC.

The above discussion, which assumes that the system is moving in free space and moreover is in thermal equilibrium, is adequate as at least a start for discussing the behavior of ^4He in the superfluid (He-II) phase. However, when we turn to the atomic alkali gases we find that they are typically confined by some kind of external (magnetic or laser) potential and, moreover, are often quite far from thermodynamic equilibrium. It is therefore necessary to generalize the idea of BEC to take account of these complications. We proceed as follows: First, suppose that the *many-body* system (assumed to be composed of N identical particles) is in a single pure state (which in general need not be an energy eigenstate) and thus is described by a wave function[10] $\Psi(\boldsymbol{r}_1\boldsymbol{r}_2...\boldsymbol{r}_N : t)$. Let us select one of the N particles—say particle 1 for definiteness—and denote its coordinate $\boldsymbol{r}$, and write the remaining $N-1$ coordinates symbolically as $\mathbf{Q}$, so that the wave function is written symbolically as $\Psi(\boldsymbol{r}, \mathbf{Q} : t)$. We then define the *single-particle density matrix* at time t, $\rho_1(\boldsymbol{r}, \boldsymbol{r}' : t)$, by the relation

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}' : t) \equiv N \int d\,\mathbf{Q}\;\Psi^*\;(\boldsymbol{r}, \mathbf{Q} : t)\;\Psi\;(\boldsymbol{r}', \mathbf{Q} : t) \tag{7}$$

In an intuitive sense, the quantity $\rho_1(\boldsymbol{r}, \boldsymbol{r}' : t)$ is as near as we can get to a description of "the behavior of a single particle averaged over that of all the others." For the case where the many-body state is a mixture, i.e. the system is in one of several orthogonal states $\Psi_n\boldsymbol{r}, \mathbf{Q} : t)$ with probability p_n, the generalization of the definition (7) is the obvious one (we just attach the same subscript n to Ψ and Ψ^* in (7), multiply by p_n, and sum over n); thus the quantity ρ_1 is uniquely defined for any many-body state.

Now, from its definition the quantity $\rho_1(\boldsymbol{r}, \boldsymbol{r}' : t)$ is Hermitian (i.e. $\rho_1(\boldsymbol{r}, \boldsymbol{r}' : t) \equiv \rho_1^*(\boldsymbol{r}', \boldsymbol{r} : t)$), and hence by a well known theorem it follows that at any time t we can find an orthonormal set of eigenfunctions $\chi_i(\boldsymbol{r}, t)$ and corresponding eigenvalues $n_i(t)$ such that ρ_1 can be written in the form

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}' : t) = \sum_i n_i(t)\chi_i^*(\boldsymbol{r}t)\chi_i(\boldsymbol{r}'t) \tag{8}$$

Eqn. (8) is quite general (we did not actually even assume that the particles involved obey Bose statistics). Note that while in the case of a translation-invariant system in thermal equilibrium the eigenfunctions $\chi_i(\boldsymbol{r}t)$ are, from symmetry, just the plane waves $V^{-1/2}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ and the n_i thus correspond to the $\langle n_k \rangle$ defined above, in general there is no simple relation between the χ_i and the eigenfunctions of the single-particle Hamiltonian, even in equilibrium. However, irrespective of this, it is clear that once the orthonormal basis $\chi_i(\boldsymbol{r}t)$ has been determined, the quantity $n_i(t)$ has the intuitive physical significance of the "average number of particles in single-particle-(like) state i at time t."

Let us now consider explicitly a Bose system, take the limit of large[11] N and consider three possible types of behavior of the quantities $n_i(t)$ in this limit:

1. All $n_i(t)$ are $0(1)$
2. One *and only one* of the $n_i(t)$ is $0(N)$, the rest $0(1)$.
3. More than one of the $n_i(t)$ are $0(N)$.

In case (1), we say we have a "normal" system; most gases and liquids composed of bosons, including liquid ^4He in the so-called He-I phase which occurs above T_λ, are believed to be normal systems in this sense. Case (3) corresponds to what is usually called "fragmented BEC"; it is unusual, but can occur under certain rather special conditions (see QL, chapter 2, section 6). The case of most interest to us in the present context is (2), which corresponds to what is sometimes called "simple BEC" or more often just "BEC," period. In this case it is conventional to denote the single macrosopic eigenvalue of ρ_1 (the "condensate number") by $N_o(t)$ and the corresponding eigenfunction ("condensate wave function") by $\chi_o(\boldsymbol{r} : t)$, and to introduce the

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[10] For pedagogical simplicity I neglect for the moment any internal (e.g. hyperfine) degrees of freedom of the particles in question.

[11] I avoid the term "thermodynamic limit" since, for example, in the case of a set of atoms confined in a harmonic trap this does not strictly exist.

order parameter $\Psi(\boldsymbol{r}t)$ by the prescription[12]

$$\Psi(\boldsymbol{r},t) \equiv \sqrt{N_o(t)}\ \chi_o(\boldsymbol{r}t) \tag{9}$$

Why do we normally assume that any BEC occuring in an interacting Bose system is of the "simple" type (case (2) above) rather than "fragmented"(case (3))? Most of the existing experimental data, both on He-II and on the alkali gases, seems consistent with this assumption, but its theoretical basis is far from trivial. One important consideration which is relevant to this question is the following: given any many-body state which is fragmented with two different macroscopic eigenvalues, it turns out that it is always possible to express it as a quantum superposition of many-body states which exhibit simple BEC (often called "coherent" states), and in many (though not all) circumstances the total energy of the fragmented states is, to an excellent approximation, the average of that of the coherent states involved. To the extent that this is true it follows that there must be at least one coherent state which has energy at least as low as that of the fragmented state; thus the latter cannot be energetically favored, and indeed barring pathology is likely to be disfavored. For a more detailed discussion, see QL Chapter 2, Section 3 and Appendix B. From now on I shall assume, unless explicitly stated otherwise that any BEC occurring in our system is of "simple" type (i.e. we have case (2), not case (3)), so that the order parameter $\Psi(\boldsymbol{r}t)$ can be defined unambiguously by eqn. (9).

Let us now turn to the question of the possibility of quantum condensation in a system of fermions. One thing is immediately clear: in view of the Pauli principle and the interpretation of the eigenvalues $n_i(t)$ of the single-particle density matrix ρ_1 as "the average number of particles in single-particle state i", none of the $n_i(t)$ can ever exceed 1; this conclusion is completely independent of the nature of any confining potential, the presence or absence of interparticle interactions or whether the system is in thermal equilibrium. Consequently, we conclude that for a Fermi system only case (1) above can occur, i.e., BEC as we have defined it is impossible.

However, that is by no means the end of the story. Let us recall that all the (non zero-mass) bosons which occur in real life are actually complexes of an even number of fermions; e.g. the ^4He atom is actually a 6-fermion complex. Let's then consider the following thought-experiment:[13] We imagine a pair of identical fermions of spin 1/2, with an interaction potential which is overall attractive in the s-state and whose strength can be tuned by adjusting some parameter. If the attraction is sufficiently strong, the pair will be able to form a diatomic molecule with $\ell = S = 0$ (with a radius a_s equal[14] to the (positive) scattering length), while if it is too weak the molecular state will not be bound but the zero-energy s-wave scattering length a_s will be negative. Consider now a large number N of such fermions in a larger volume V; we will take the usual thermodynamic limit and denote by $n \equiv N/V$ the total fermion density in this limit, so that the average interparticle spacing is $\sim n^{-1/3} \equiv r_o$. Suppose we start by setting the attractive potential to be strong, so that the radius a_s of the resulting molecule is $\ll r_0$. Then it is overwhelmingly plausible that the groundstate of the N-particle system corresponds to the fermions having paired off to form $N/2$ diatomic molecules, and since these molecules behave as bosons they should be Bose-condensed; in fact, in the limit $a_s \ll r_0$ these molecules should be virtually noninteracting, and we might therefore guess that N_o (as defined above for bosons) would be approximately equal to $N/2$. This limit is known in the literature as the "BEC limit."

How would we describe this state of affairs explicitly in terms of the *fermions*? The many-body wave function $\Psi(\boldsymbol{r}_1\sigma_1, \boldsymbol{r}_2\sigma_2 ... \boldsymbol{r}_N\sigma_N)$ must, of course, be it antisymmetric under exchange $\boldsymbol{r}_i\sigma_i \leftrightarrows \boldsymbol{r}_j\sigma_j$ (where σ_i is the projection of the spin of the i-th fermion on some conventionally chosen axis), and for the simple case $N = 2$ this is automatically satisfied by the $\ell = S = 0$ groundstate, which is of the form (in an obvious notation)

$$\begin{aligned}\Psi(\boldsymbol{r}_1\sigma_1\boldsymbol{r}_2\sigma_2) &= 2^{-1/2}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)\cdot f(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \\ &\equiv \varphi(\boldsymbol{r}_1\boldsymbol{r}_2 : \sigma_1\sigma_2) \end{aligned}\tag{10}$$

When we assume f is normalized to unity, the ansatz for the many-body groundstate which corresponds to the hypothesis of Bose condensation

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[12] Alternative definitions of the order parameter are common in the literature; their advantages and disadvantages are discussed in QL Chapter 2, Section 2.

[13] Which in the last three years has actually been realized to all intents and purposes in the laboratory, see QL, chapter 8, section 4.

[14] I assume for simplicity that a_s is large compared to the physical range of the potential.

of the molecules with $N_o = N/2$ is, apart from normalization

$$\begin{aligned}&\psi(\boldsymbol{r}_1\sigma_1, \boldsymbol{r}_2\sigma_2 ... \boldsymbol{r}_N\sigma_N)\\ &\quad = \mathcal{A}\varphi(\boldsymbol{r}_1\boldsymbol{r}_2, \sigma_1\sigma_2)\varphi(\boldsymbol{r}_3\boldsymbol{r}_4\sigma_3\sigma_4)\\ &\qquad ....\varphi(\boldsymbol{r}_{N-1}\boldsymbol{r}_N\sigma_{N-1}\sigma_N) \quad (11)\end{aligned}$$

where $\mathcal{A}$ denotes the operation of antisymmetrization not only within a bracket ( ) (already implemented automatically by the form of φ); but also *between* brackets, e.g. under the interchange $\boldsymbol{r}_1\sigma_1 \rightleftarrows \boldsymbol{r}_3\sigma_3$. Actually, for the reason given in section 2, in this limit the effects of antisymmetrization "between brackets" is negligible, because the physical probability amplitude for two single fermions to exchange their partners is vanishingly small[15], and hence the representation of the system as a system of $N/2$ condensed bosons is entirely legitimate.

Let us, nevertheless, ask whether we can define a property (other than the wave function itself) which explicitly refers to the *fermions* and characterizes the "condensed" nature of the system. The obvious quantity to look at is the one which for $N = 2$ simply reduces to the 2-particle wave function, namely the *two-particle density matrix* ρ_2. To define this quantity, we proceed analogously to the Bose case; that is, we pick out arbitrarily two particles, say for definiteness 1 and 2, indicate the coordinates and spins of the remaining $N-2$ particles by $\boldsymbol{Q}$ (so that $\int d\,\boldsymbol{Q}$ indicates both an integration over $N-2$ coordinates and a sum over $N-2$ spins) and define

$$\begin{aligned}&\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2\sigma_1\sigma_2 : \boldsymbol{r}'_1\boldsymbol{r}'_2\sigma'_1\sigma'_2 : t)\\ &\quad \equiv N(N-1)\int d\boldsymbol{Q}\Psi^*(\boldsymbol{r}_1\boldsymbol{r}_2\sigma_1\sigma_2 : \boldsymbol{Q} : t)\\ &\qquad \Psi(\boldsymbol{r}'_1\boldsymbol{r}'_2\sigma'_1\sigma'_2 : \boldsymbol{Q} : t) \quad (12)\end{aligned}$$

Analogously to the Bose case, ρ_2 is intuitively our best description of the "behavior of a pair of particles averaged over that of the $N-2$ other particles in the system". If we evaluate expression (12) with Ψ given by the (time-independent) ansatz (11), we find after some labor (taking account of the correct normalization, etc.) that

$$\begin{aligned}&\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2\sigma_1\sigma_2 : \boldsymbol{r}'_1\boldsymbol{r}'_2\sigma'_1\sigma'_2 : t)\\ &\quad = (N/2)\cdot\varphi^*(\boldsymbol{r}_1\boldsymbol{r}_2\sigma_1\sigma_2 : t)\ \varphi\ (\boldsymbol{r}'_1\boldsymbol{r}'_2\sigma'_1\sigma'_2 : t)\\ &\qquad + \rho'_2 \quad (13)\end{aligned}$$

where all the eigenvalues of ρ'_2 are 0(1). Thus ρ_2 has a single macroscopic ($N_0 \sim N$) eigenvalue, and the corresponding eigenfunction is just that of the composite bosonic molecule. Note that the antisymmetrization "between brackets" is automatically taken care of in definition (12), and does not appear explicitly in (13).

So far, we do not appear to have gained anything much by writing things explicitly in terms of the component fermions: all the physical properties of the system in this limit are just those of a set of condensed composite bosons. However, let us now imagine that we gradually turn down the strength of the inter-fermion potential. As we do so, the molecular radius a_s becomes larger and larger, and eventually becomes comparable to the interparticle spacing r_o (or the "intermolecular" spacing $2^{1/3}r_o$). At this point our argument that the effects of "inter-bracket" antisymmetrization are negligible fails, and independently of that the interaction between fermions on "different" molecules becomes appreciable. Indeed, by this time it has become impossible to say which is the unique "partner" of any given fermion. If we weaken the interaction yet further, we eventually reach the point at which a single fermion pair no longer forms a molecule (but the magnitude of the s-wave scattering length a_s is large (actually infinite!) compared to r_o); this point is often called the "unitarity limit" in the literature. At this point a_s changes sign, going from $+\infty$ to $-\infty$. Weakening the interaction further still, we finally reach a situation where the s-wave scattering length, while negative, is much less than the interparticle spacing r_o; for a reason we shall see below, this limit is often referred to as the "BCS limit."

Now, once we have departed appreciably from the "BEC limit" $r_o \gg a_s > 0$ it is clear that we would not necessarily expect the simple ansatz (11) for the many-body wave function to be even qualitatively correct. Nevertheless, we can still define the two-particle density matrix by eqn. (12), and inquire whether it still has a single macroscopic eigenvalue. Remarkably, both theoretical arguments and the experimental evidence newly attained in recent studies of the Fermi alkali gases suggest that, at least for a class of "reasonable" potentials, the answer is yes, not only in the regime $a_s > 0$ (when the two-particle state is bound) but

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[15] Each of the fermions would have to tunnel a distance $\sim r_o$ with a negative energy $\sim \hbar^2/ma_s^2$; the WKB exponent for this process is $\sim r_o/a_s \gg 1$. Configurations in which the COM's of the two molecules are $\lesssim a_s$ apart have a probability $\sim (a_s/r_o)^3 \ll 1$.

even for $a_s < 0$, when there is no 2-particle bound state! Indeed, if we take the limit $-a_s \to 0$ (and replace the atoms by electrons) we reach precisely the system studied by Bardeen, Cooper and Schrieffer in their famous 1957 paper on superconductivity; in this limit (the limit of "almost-free" fermions subject to a weak two-particle attraction) it is almost universally believed that the groundstate indeed corresponds to a ρ_2 which has a single macroscopic eigenvalue "of order" N. However, while in the BEC limit the ratio N_o/N is 1/2, in this "BCS" limit it is exponentially small: in fact, for a two-body potential parametrized by an s-wave scattering length a_s, the BCS formula for N_o is

$$N_o/N \sim exp - \pi/(2k_F a_s) \tag{14}$$

where $k_F \equiv (3\pi^2 n)^{1/3}$ is the Fermi wave vector of the free Fermi gas. Correspondingly, it is believed that the transition temperature to the "quantum-condensed" state ($N_o(T) \sim N$) which in the BEC limit would be expected to be given by formula (5) (with m twice the fermion mass) and thus to be of the order of the Fermi temperature $T_c \equiv \hbar^2 k_F^2/2mk$, is in the BCS limit suppressed relative to T_F by the same exponential factor as in (14).

In the following we will consider arbitrary states (not necessarily thermodynamic equilibrium ones) of a Fermi system which are characterized by the fact that the two-particle density matrix $\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2\sigma_1\sigma_2 : \boldsymbol{r}'_1\boldsymbol{r}'_2\sigma'_1\sigma'_2 : t)$ has *one and only one*[16]eigenvalue of order N (i.e. which are analog of case (2) for the Bose system). For such cases, we denote this single macroscopic eigenvalue $N_o(t)$ and call it the "condensate number"; the corresponding eigenvalue will be denoted $\chi_o(\boldsymbol{r}_1\boldsymbol{r}_2\sigma_1\sigma_2 : t)$ and called the "wave function of the condensate" (or "wave function of the Cooper pairs", cf. below). Finally, we can introduce an order parameter for the Fermi system by the prescription (the notation F rather than Ψ for this quantity has become conventional)

$$F(\boldsymbol{r}\sigma, \boldsymbol{r}'\sigma' : t) \equiv \sqrt{N_o(t)}\; \chi_o(\boldsymbol{r}\boldsymbol{r}'\sigma\sigma' : t) \tag{15}$$

The "objects" which are described by the function F are *pairs* of particles, and are often referred to as "Cooper pairs." We can rewrite (15) in terms of the "center-of-mass" and "relative" coordinates of the pair, $\boldsymbol{R}\ \boldsymbol{\rho}$:

$$F(\boldsymbol{r}\sigma, \boldsymbol{r}'\sigma' : t) \equiv F(\mathbf{R} : \boldsymbol{\rho}, \sigma, \sigma' : \boldsymbol{t}) \tag{16}$$

In the simplest cases ("classic" (BCS) superconductors and the Fermi alkali gases so far investigated experimentally) we can write $F(\mathbf{R} : \boldsymbol{\rho}, \sigma\sigma')$ in the approximate form

$$F(\mathbf{R} : \boldsymbol{\rho}, \sigma\sigma' : t) \cong \Psi(\mathbf{R}, t) f(\boldsymbol{\rho}, \sigma\sigma') \tag{17}$$

where the "internal" (relative) wave function of the pair has the form of an s-wave spin singlet, i.e.

$$f(\boldsymbol{\rho}, \sigma, \sigma') = 2^{-1/2}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2) f(|\boldsymbol{\rho}|) \tag{18}$$

where the actual form of $f(|\boldsymbol{\rho}|)$ is fixed by the energetics and is thus not free to vary in an interesting way. In such a case all the "interesting" behavior of the system is associated with the function $\Psi(\boldsymbol{R}, t)$ which is, in effect, the center-of-mass wave function of the pairs and turns out, up to normalization, to be nothing but the celebrated "macroscopic wave function" introduced long ago by Ginzburg and Landau on the basis of phenomenological arguments. In some other cases (superfluid ^3He and probably the cuprate superconductors) the "internal" part of the wave function is not uniquely fixed by the dynamics and may itself be a function of time; for example, the superfluid A phase of liquid ^3He is believed to correspond to pairing in a spin triplet state with projection zero on some axis $\boldsymbol{d}$ and with apparent angular momentum $\hbar$ around some axis $\hat{\boldsymbol{\ell}}$, so that if we chose this axis as the z-axis and suppose for simplicity that it and the overall amplitudes are constant in space and time we have schematically

$$F(\boldsymbol{\rho}, \sigma, \sigma') = const.\ 2^{-1/2}(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)_{\boldsymbol{d}}\; f\,(|\boldsymbol{\rho}|) \sin\,\theta\; e^{i\varphi} \tag{19}$$

with θ and φ the spherical polar angles of $\boldsymbol{\rho}$. In the more general case the axis $\hat{\boldsymbol{\ell}}$ (and the axis $\boldsymbol{d}$ associated with the spin state) may itself vary in space and time.

4. Effects of condensation

In the rest of this paper I shall discuss, at a qualitative level, the principal effects peculiar to a quantum condensate. All of them are in the last resort consequences of the fact that a nonzero fraction of all the particles (in a Bose system) or of all the pairs of particles (in a Fermi system) are in *the same single-particle/two-particle quantum state*, and that this is true not only in global thermal equilibrium but also for states which are "sufficiently close" to (stable or metastable) equilibrium. A useful way of displaying this feature is

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[16] Just as in the Bose case, the reason why "fragmented" states are rare is quite subtle: see QL pp. 207–8.

to define, as above, a condensate wave function (order parameter) and to write the free energy as a functional of this order parameter. In the simplest case (a spinless Bose system such as liquid ^4He, or the classic superconductors) the OP is in effect the COM wave function[17] of the condensate atoms/pairs and is a complex scalar $\Psi\ (\boldsymbol{R})$: in this case, in the absence of electromagnetic gauge coupling, the free energy functional has the form (we replace $\boldsymbol{R}$ by $\boldsymbol{r}$ for clarity)

$$F\{\Psi(\boldsymbol{r}):T\} \;=\; \int d\boldsymbol{r}\ \Big\{\mathcal{F}_o(T)-\alpha(T)|\Psi(\boldsymbol{r})|^2 + \frac{1}{2}\beta(T)|\Psi(\boldsymbol{r})|^4 \;+\; \gamma(T)|\underset{\sim}{\nabla}\Psi|^2\Big\} \tag{20}$$

with the coefficients $\alpha(T), \beta(T), \gamma(T) > 0$. With such a free energy functional, it is clear that deviations from the equilibrium order parameter $\Psi(\boldsymbol{r}) = \sqrt{\alpha(T)/\beta(T)}\ e^{i\delta}$ ($\delta = \mathrm{const}$) in either phase or amplitude are energetically disfavored.

The most directly visible effect of condensation is the behavior of the spatial density distribution of a dilute Bose gas such as ^{87}Rb confined in a 3D harmonic trap (frequency ω_o). In such a trap the unique quantum-mechanical groundstate for a single particle has energy $\frac{3}{2}\hbar\omega_o$ and is spread over a linear dimension $a_{zp} \sim (\hbar/m\omega_o)^{1/2}$ which is typically $\sim 1\mu$. The transition temperature T_c of a gas of N atoms to the BEC state is $\sim N^{1/3}\hbar\omega_o/k_B$, so at temperatures a little above this the width r_{th} of the density distribution in real space, which is given by $\frac{1}{2}m\omega_o^2 r_{th}^2 \sim k_B T$, is of order $N^{1/6}a_{zp}$; since typically $N \sim 10^6$ this is $\gg a_{zp}$. Now let us ask what happens below T_c, when BEC sets in. If the gas was completely noninteracting, a nonzero fraction (tending to 1 as $T \to 0$) of all the atoms would immediately concentrate, according to (the appropriate generalization of) eqn. (6), in the groundstate, so that one would see a huge spike in the distribution with width $\sim a_{zp}$. In real life, most alkali gases have a repulsive interaction between the atoms, which tends to broaden the peak to a few times a_{zp}; however, the effect is still quite spectacular, see e.g. [1].

A second characteristic consequence of quantum condensation is various macroscopic interference effects, of which the best-known is that seen in the celebrated experiment of [2]. In this experiment ^{87}Rb atoms were independently trapped and induced to undergo BEC in two different potential wells separated by a laser barrier so high that the probability of one atom tunnelling through the barrier (or surmounting it by thermal activation) is completely negligible. The barrier was then removed, so that the two atomic clouds could expand and overlap, and the density distribution studied by the absorption of a laser beam. The experimental data are spectacular: on each individual run of the experiment a pattern of alternating high- and low-density regions (stripes) is seen, but the offset (i.e., the absolute position of a given high-density stripe) varies at random from run to run. This behavior can be understood qualitatively as follows: If we had a set of N atoms all condensed into the same single-particle state, and the latter were a quantum superposition of states originating from the left and right well respectively, with a definite relative phase $\Delta\varphi$ ("coherent states"), then we should expect to see an interference pattern with an offset which is a linear function of $\Delta\varphi$. In reality, the initial state of the gas is "fragmented": we have roughly $N/2$ atoms in well 1 and another $N/2$ in well 2. However, as mentioned above, any such state can be expressed as a quantum superposition of a set of coherent states with different $\Delta\varphi$, and according to the standard quantum theory of measurement, when we attempt to "measure" $\Delta\varphi$ by looking at the interference pattern, we will pick out just one member of the superposition, i.e. one particular value of $\Delta\varphi$. For a detailed discussion, see QL Chapter 4, Section 5.

Next, let us discuss the Josephson effect. Imagine a single electron which is able to move between two "boxes" L and R, in each of which it has a fixed wave function Ψ_L, Ψ_R (let us say for definiteness the groundstate in the box in question). The matrix element for tunnelling between the boxes is t_o, and a dc voltage V is applied between them. By writing the total wave function of the electron in the form

$$\Psi(t) = a(t)\Psi_L + b(t)\Psi_R \quad (|a(t)|^2 + |b(t)|^2 = 1) \tag{21}$$

and solving the Schrödinger equation for the coefficients $a(t), b(t)$, it is straightforward to obtain the result that in the limit $eV \gg t_o$ the electric current between the boxes L and R has the form

$$I(t) = \mathrm{const.}\ \mathrm{t_o}\ \sin\{(\mathrm{eV}/\hbar)\mathrm{t} + \delta\} \tag{22}$$

(when the constant δ is determined by the relative phase of a and b at $t = 0$). Note that the derivation

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[17] In the case of a simple Bose gas this wave function is called the Gross-Pitaevskii wave function (OP), in the case of a Fermi system with s-wave pairing the Ginzburg-Landau wave function.

of this result implicitly assumes that the ground-state energies E_L, E_R in boxes L and R are identical. Were this not the case, or were we to consider a superposition of (different) excited states in L and R respectively, then there would be an extra term added to the argument of the time-dependence in (22): $\dot{e}V \rightarrow eV + \Delta E$

Now, in the case of two real metals separated by (say) a tunnel oxide barrier we have, of course, many electrons, and in general each electron (fermion) will occupy a different linear combination of states in L and R: schematically,

$$\Psi(t) = a(t)\Psi_{Li} + b(t)\Psi_{Rj} \tag{23}$$

so that the energy ΔE is a function of i and j. Here we expect for the total current, again very schematically,

$$I(t) = \text{const} \sum_{\text{ij}} \text{t}_{\text{ij}} \sin\left\{\left(\text{eV} + \Delta\text{E}_{\text{ij}}\right) \text{t}/\hbar + \delta_{\text{ij}}\right\} \tag{24}$$

In view of the randomness of the "extra" phases $\Delta E_{ij} t/\hbar$, expression (24) vanishes to lowest order in t_{ij}, and a (considerably more careful) calculation shows that the correct expression for $I(t)$ corresponds $\underline{\text{to a}}$ simple ohmic conductance proportional to $\overline{|t_{ij}|^2}$.

Suppose, however, that we were dealing not with fermions but with bosons, and the latter are Bose-condensed. In that case all the condensed particles would occupy *a single* one-particle state of the form (21), and the result (22) would immediately follow. Although this behavior has not (to my knowledge) been seen directly in a bosonic system, effects closely related to it have been known for many years in liquid ^4He, and other related effects have very recently been seen in alkali atomic gases. However, the original Josephson effect is seen most clearly in superconducting metals. In this case it is not the single electrons but the Cooper pairs which are in a linear superposition of states in the L and R boxes: schematically, the "COM pair wave function" $\Psi(\boldsymbol{R}, t)$ (see eqn. (17)) has the form

$$\Psi(\boldsymbol{R}t) = a(t)\Psi_L + b(t)\Psi_R \tag{25}$$

The argument leading to (22) then goes through exactly as in the single-electron case, with the differences that (a) t_o is replaced by the tunnelling amplitude for a *pair* and (b) the single-electron charge e is replaced by the pair charge $2e$. Thus we obtain the standard result[18] for the dc Josephson effect

$$I(t) = I_c \ \sin\{(2eV/\hbar)t + \delta\} \tag{26a}$$

(where I_c is proportional to the pair tunnelling matrix element). The dc Josephson effect is formally obtained by setting $V = 0$:

$$I = I_c \sin\delta \tag{26b}$$

where δ is the (time-independent) relative phase of a and b in (2δ).[19]

The Josephson effect, as it occurs in classic superconductors, is a consequence of the requirement that the *center-of-mass* wave function $\Psi(\boldsymbol{R}, t)$ (eqn. 17) should be identical for all the Cooper pairs; since these systems have simple s-wave pairing, the internal structure of the pair is fixed by the energetics and thus is automatically identical for all and not readily variable, so it does not give rise to any particularly interesting effects. The situation is more interesting in the superfluid phases of liquid ^3He, a system in which the pairs have nontrivial internal ("orientational") degrees of freedom associated with the spins and relative orbital angular momenta; serendipitously, it turns out that these orientational degrees of freedom are controlled only by very weak forces and thus can show a rich pattern of dynamical behavior. Let us consider specifically the question: Given that two ^3He nuclei have their spins oriented in (say) the positive z-direction, what is the optimum relative *orbital* configuration? Of course, to the extent that the Hamiltonian is invariant under *relative* rotation of the spin and orbital coordinate systems, the answer is that all orbital configurations are degenerate. If we now take into account the interaction between the nuclear magnetic dipole moments, then just as for two macroscopic bar magnets it favors the "end-over-end" configuration rather than the "side-by-side" one (see fig. 1); for two nuclei in a state of definite relative angular momentum, the corresponding statement is that angular momentum in the xy-plane is favored over that along the z-axis. However, the energy involved (call it g_D) is very tiny (even at the distance of closest approach of two ^3He atoms it is less than $10^{-7}K$), and hence

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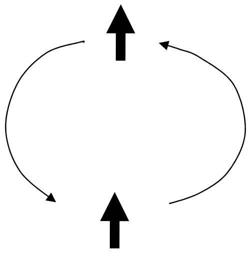
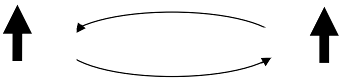
[18] The quantity ΔE can usually be neglected in the limit of large volumes of the two bulk metals; otherwise, it adds to the $2eV$ as above.

[19] However, for this result to make sense we need to provide external leads to prevent accumulation of charge.

at currently attainable temperatures ($\gtrsim 10^{-3}K$) it is swamped by the thermal energy, so that in normal liquid ^3He two ^3He atoms selected at random are as likely (to within one part in 10^4) to be in the "side-by-side" configuration ($\boldsymbol{\ell} \parallel \boldsymbol{z}$) as in the "end-over-end" one.



"good"



"bad"

FIG. 1: "good" and "bad" relative positions (or rotations) for two nuclear spins in liquid ^3He.

Now let us consider what happens when Cooper pairs are formed in the liquid. The crucial point is that, as a result of the "strong" forces in the problem (kinetic energy and the hard-core and van der Waals potential energies) *all Cooper pairs must be in the same two-particle state*, not only as regards their center-of-mass behavior but also as regards their relative behavior, i.e. the relative orientation of their spins and orbital angular momenta. So now if we assume that the pairs form with both spins either parallel ($\uparrow\uparrow$) or antiparallel ($\downarrow\downarrow$) to the z-axis (this is the case for the A phase in an external magnetic field along the z-axis, so as to allow the maximum polarizability), then crudely speaking the system has to choose between having *all* pairs having angular momentum along the z-axis, or all having it in some common direction in the xy-plane. The difference in energy between these two configurations is now not g_D, but rather $N_o g_D$, where N_o is the "number of Cooper pairs" which is proportional to N. The resulting energy difference is $\sim 10^{20} g_D$ and thus very much larger than the thermal energy $k_B T$, so the system in equilibrium will always realize the "good" configuration (angular momentum in xy-plane): the actual direction within this plane has to be fixed by further considerations, typically connected with the shape of the sample.

Rather than fix the spins and ask about the dependence of the energy on the direction of angular momentum (or equivalently the orbital coordinates) we could of course equally well turn the question around: that is, we keep the (common) orbital coordinates of the pairs fixed and ask about the dependence of the energy on the spin coordinates. In particular, it turns out that in the so-called A phase of superfluid ^3He the spin structure of the pair corresponds to total spin $S = 1$ and spin projection zero along some axis $\boldsymbol{d}$ (cf. eqn. (19)), which in equilibrium lies along the (unique for this phase) direction $\boldsymbol{\ell}$ of the orbital angular momentum.[20] Now it turns out that if we apply an external magnetic field $\boldsymbol{H}$ over a timescale so short that the magnetization of the system has no time to adjust to it (so that the system is out of equilibrium), the effect is to rotate not only the total spin $\boldsymbol{S}$ but also the quantization axis $\boldsymbol{d}$ of the pairs around the direction of the field. As a result, the dipole energy is no longer minimized, and the efforts of the system, as it were, to restore the minimum value lead to a rich spin dynamics. In particular, if $\boldsymbol{H}$ is along the z-axis then $\boldsymbol{d}$ will precess in the xy-plane, and as we have mentioned[20] this corresponds to a precession of the relative phase of the $\uparrow\uparrow$ and $\downarrow\downarrow$ pairs, at a rate governed by the field[21] $\boldsymbol{H}$. Thus the situation is closely analogous to that in the simple Josephson effect, with the spin-up and spin-down populations playing the role of the electrons in the bulk systems L and R respectively, and since the energy contains a term (in the present case the nuclear dipole energy) which is sensitive to the relative phase of the pairs in the two "regions," a current is driven between them; in this case the result is a time-dependent spin polarization $S_z(t)$. Indeed, in the limit of high field ($H \gg \hbar\omega_o/\mu$, where $\omega_o \equiv (N_C g_D/\chi)^{1/2}$) we find the precise analog of the Josephson effect, with the spin polarization oscillating at the "Josephson fre-

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[20] A value of $\boldsymbol{d}$ in the xy-plane corresponds to pairing of $\uparrow\uparrow$ and $\downarrow\downarrow$ with some definite relative phase which is a function of the direction of $\boldsymbol{d}$.

[21] Or more accurately by its "nonequilibrium part" $\boldsymbol{H} - \boldsymbol{S}/\chi$, where χ is the static susceptibility.

quency" $2\mu H/\hbar$ (compare eqn. (26a)). At lower fields it is necessary to take into account that the "effective" field $H - S_z/\chi$ is itself time-dependent[22] through $S_z(t)$; the result for small H is a simple harmonic oscillation at frequency ω_o, the so-called longitudinal resonance.

Because of the three-dimensional nature of the spin degree of freedom, the longitudinal resonance by no means exhausts the interesting spin dynamics of the $^3He - A$ phase; the resonance in the conventional geometry (when the rf field is perpendicular to the external one) is also affected. In the B phase the situation is even more interesting: since in that phase the dipole energy is unaffected by (small) rotations around any axis in the xy-plane, there is no effect on the transverse resonance. However, the dipole energy *is* effected by (even small) rotations around the z-axis, and as a result one gets a spectacular *longitudinal* resonance. For details see QL, Chapter 6, Section 4.

Let us finally turn to what was for many years the only obvious (in retrospect!) manifestation of quantum condensation, and is still perhaps the most spectacular one, namely the complex of phenomena which goes under the name of superfluidity (when it occurs in a neutral system) or superconductivity (when found in the electrically charged system of electrons in metals). I would like to stress that both "superfluidity" and "superconductivity" are indeed a *complex* of phenomena, which are commonly found to occur together but do not necessarily do so under all possible conditions; hence, questions like "what are the necessary and sufficient conditions for superfluidity?" can be ambiguous and misleading in the absence of a precise specification of exactly which phenomena are included in the definition.[23]

The main ingredients in the complex of phenomena known as superfluidity/superconductivity are two superficially similar but fundamentally very different ones: the *metastable* phenomenon of persistent currents, and the *thermodynamic equilibrium* effect which in neutral systems is known as nonclassical rotational inertia (NCRI) or the Hess-Fairbank effect, and in charged systems is the diamagnetism underlying the Meissner effect. It cannot be overemphasized that while these two phenomena very commonly go together, they are conceptually very different, and neither logically implies the other. I will now attempt to amplify this crucial point.

It is simplest to consider the annular geometry shown in fig. 2, when the thickness d of the ring is small compared to the mean radius R, so that corrections of order d/R to the formulae obtained below may be safely neglected. We define a "characteristic quantum unit of angular velocity" ω_C by the formula (m = mass of particles in question)

$$\omega_C \equiv \hbar/mR^2 \tag{27}$$

so that the kinetic energy of angular motion of a single particle is $\ell^2\hbar\omega_C$ with $\ell = 0, \pm1, \pm2...$ the angular momentum quantum number. We now consider two quite different effects, for the moment in an electrically neutral system such as ^4He:

1. Imagine that we rotate the annular container *very slowly*, in fact with an angular velocity $\omega < \frac{1}{2}\omega_C$. Above the temperature of the transition to the superfluid state (in the case of ^4He conventionally denoted T_λ) the liquid will rotate exactly with the container[24], so that its total angular momentum $\boldsymbol{L}$ is $I_{cl}\boldsymbol{\omega}$ when $I_{cl} \equiv NmR^2$ is the classical moment of inertia. However, once the temperature falls below T_λ the angular momentum decreases even though the container is still rotating: we find a *temperature-dependent* value given by

$$L(T) = f_n(T)\; I_{cl}\omega \tag{28}$$

where the so-called "normal fraction" $f_n(T)$ decreases smoothly from 1 at $T = T_\lambda$ to 0 at $T = 0$; thus, at $T = 0$ the liquid appears to be stationary in the laboratory frame[25] even though the container is still rotating.

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[22] A similar effect (the "Josephson plasma resonance") can occur in the superconducting case if the combined $L - R$ system is open-circuited.

[23] In particular, discussions of "superconductivity" in textbooks on elementary particle physics (where it is routinely invoked as a condensed-matter analog of the Higgs mechanism) often give the impression that it is synonymous with the Meissner effect (on which see below) and/or that the phenomenon of persistent currents is equivalent to that effect; this seems to the present author extremely misleading.

[24] It will form the usual meniscus, but the effects of this are of higher order in d/R and can consistently be neglected.

[25] Or more strictly (in a suitable geometry) in the frame of the fixed stars.

This is the effect usually known as nonclassical rotational inertia (NCRI) or the Hess-Fairbank effect: it is a true *thermodynamic equilibrium* phenomenon, not a consequence of "vanishing viscosity" (the latter circumstance would prevent the liquid from coming into equilibrium with the walls, but once equilibrium is attained (above T_λ) there is no way it could cause it to come *out* of equilibrium with them!)

2. Now consider a different experiment: Initially, we keep the liquid in the normal phase ($T > T_\lambda$) and rotate the container at some "large" angular velocity ω (typically, $\sim 10^4 \omega_C$); the liquid then comes, just as would water, into equilibrium with the rotating container. Next, while still rotating the container at angular velocity ω, we cool through T_λ. Although we shall see below that there is, in general, a slight change in the angular velocity of the liquid (at $T = 0$ it in fact rotates at angular velocity $n\omega_C$, where n is the nearest integer to ω/ω_C), this is of order ω_C/ω and typically negligible in practice, so that to all intents and purposes the liquid appears, just as in the normal phase, to be rotating with the container. Now we stop the container and observe the final state of the liquid. What we find is that even in the limit of long times (much longer than any plausible "relaxation time" for container-liquid equilibration) part of the liquid appears to continue to rotate with angular velocity ω; more explicitly, the angular momentum $\boldsymbol{L}$ is given by the formula

$$\boldsymbol{L} \cong f_s(T) I_{cl} \boldsymbol{\omega} \tag{29}$$

where the "superfluid fraction" $f_s(T)$ is related to the "normal fraction" $f_n(T)$ defined in connection with eqn. (28) by

$$f_s(T) = 1 - f_n(T) \tag{30}$$

By raising and lowering the temperature (but always staying below T_λ) we can *reversibly* alter the value of L, even though the container is now stationary. It cannot be overemphasized that the state we are seeing in this experiment cannot possibly be the thermal equilibrium one[26]; rather we have an example of a spectacular degree of *metastability*, which I will refer to as the phenomenon of "persistent currents".

The above discussion refers to a neutral system. In the case of an electrically charged system it is clear that the description of the phenomenon of persistent currents is essentially unchanged: a current set up in a superconducting loop will persist indefinitely, even though it cannot possibly correspond to the equilibrium state of the system. As regards the NCRI experiment (1) something similar should occur in a superconducting metal.[27] However, what is normally regarded as the analog of NCRI for a charged system is the phenomenon of *diamagnetism.* To introduce this, we note the fact that the behavior of a charged system in an applied transverse vector potential $\boldsymbol{A}$ (or the corresponding magnetic field $\boldsymbol{B}$) with the walls at rest is precisely analogous to that of a neutral system when the walls are rotating at angular velocity $\boldsymbol{\omega}$, provided that the latter is viewed not from the laboratory frame of reference but from that of the rotating walls, with the correspondence $\omega \to eB/2m$. Thus, in particular, the analog of the statement that in any "normal" phase the neutral system rotates with the walls is the statement that application of a magnetic field to a charged system in the normal phase will produce no current in the lab frame. Conversely, the analog of the statement that in the "superfluid" phase part of the neutral system is stationary in the lab frame (hence moving as viewed from that of the walls) is that application of a vector potential to the "superconducting" system results in a non-zero current, whose sign is diamagnetic, i.e. such that the resulting field tends to screen out the external one. The quantitative statement of this effect, first written down by F. London, is

$$\boldsymbol{J} = - \wedge (T) \boldsymbol{A} \tag{31}$$

$$\wedge(T) = (ne^2/m) f_S(T) \tag{32}$$

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[26] In fact, it is easy to demonstrate that in the considered geometry the maximum possible value of the angular momentum in equilibrium with walls stationary is $I_{cl}\omega_C/2$.

[27] But in a bulk geometry is complicated by the Meissner effect (see below).

when n is the density of electrons and $f_S(T)$ the superfluid fraction (which, of course, need not be numerically the same function of temperature as in the neutral case (since in general the microscopic nature of the systems is different), but retains the property that $f_S(0) = 1$ and $f_S \to 0$ at the transition to the normal phase). When combined with the familiar Maxwell's equations. Eqn. (31) leads to the *Meissner effect*: an externally applied magnetic field will be screened out of the body of a superconducting metal over a length scale of the order of the London penetration depth λ_L given by

$$\lambda_L^{-2} = ne^2\mu_o/m \tag{33}$$

λ_L is typically $\sim$ a few hundred Å, so that from a macroscopic point of view it looks as if the superconductor is excluding the magnetic field entirely. The Meissner effect can in some sense be regarded as the familiar phenomenon of atomic diamagnetism *writ large*; in the atomic case, while the qualitative behavior is identical, the length corresponding to λ_L is very large compared to the atomic dimension, so that the residual analog of the Meissner effect is a weak ($\sim 10^{-5}$) attenuation of the magnetic field actually seen by the nucleus by comparison with that applied externally to the atom.

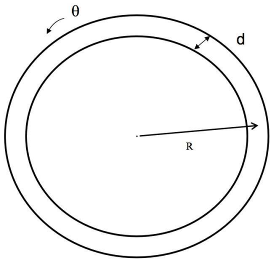


FIG. 2: Annular geometry for discussion of NCRI and persistent currents.

Let's now discuss how the two conceptually very different phenomena (1) and (2) are explained by the onset of quantum condensation. In the case of NCRI it is simplest to start with the case of a free Bose gas, where all the calculations can be carried out explicitly. The essential point is that when a system is in equilibrium with walls rotating at angular velocity $\boldsymbol{\omega}$, the effective Hamiltonian which governs the statistical distribution is not the original Hamiltonian $\hat{H}$, but rather the quantity

$$\hat{H}_{eff} = \hat{H}_o - \boldsymbol{\omega} \cdot \hat{\boldsymbol{L}} \tag{34}$$

where $\hat{L}$ is the angular momentum operator. Thus, in particular, the "effective" kinetic energy of angular motion of a particle with angular momentum quantum number ℓ is

$$E_{eff}(\ell) = \frac{\ell^2}{2}\hbar\omega_c - \hbar\omega\ell \tag{35}$$

Consider first the normal (i.e. non-Bose condensed) phase. In the Maxwell-Boltzmann limit the distribution of particles between the different ℓ-values is given simply by

$$n_\ell(T) = c(T)\exp - \left(\frac{\ell^2}{2}\hbar\omega_c - \hbar\omega\ell\right)/kT \tag{36}$$

where the constant is such that

$$\sum_\ell n_\ell(T) = N \tag{37}$$

The total angular momentum is given by the formula

$$L = \hbar\sum_\ell \ell n_\ell(T) \tag{38}$$

In evaluating expression (38) it is important to bear in mind that under all experimental conditions attained to date (or likely to be attained in the foreseeable future) the rotational energy quantum $\hbar\omega_C$ is very small (typically $\sim 10^{-7}$) relative to the thermal energy k_BT. This justifies the replacement of the sum in (38) by an integral, and we easily find

$$L = N\hbar(\omega/\omega_c) \equiv I_{cl}\omega \tag{39}$$

The liquid therefore rotates exactly with the container, as expected (fig. 3a). At lower temperatures (but still above the BEC onset temperature T_c) the argument needs to be modified somewhat (since the Bose distribution, unlike the MB one, does not allow us to factor out the dependence on ℓ), but the result is the same.

Now consider the behavior in the BEC phase ($T < T_c$). While the uncondensed particles continue to behave as in the normal phase, the condensate must form in the (unique) single-particle state with the lowest effective energy, namely, with the ℓ-value which minimizes expression (35)[28]. This is

$$\ell_o \equiv \text{int.}\ (\omega/\omega_c - 1/2) \qquad (40)$$

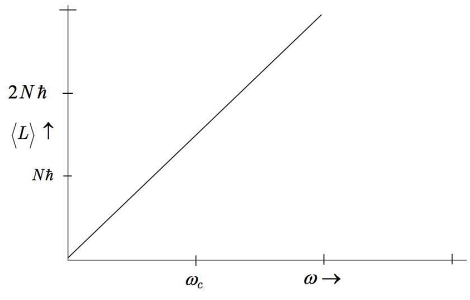
and the resulting contribution to the angular momentum is $Nf_o(T)\ \hbar\ell_o$, where $f_o(T) = N_o(T)/N$ is the condensate fraction at the temperature in question. Thus the total angular momentum at temperature T is given by

$$L = (1 - f_o(T))I_{cl}\omega + f_o(T)I_{cl}\ell_o\omega_c \qquad (41)$$

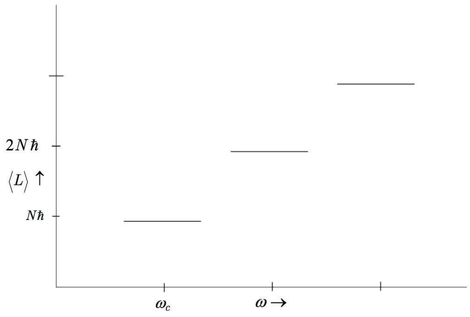
In particular, for $\omega < \frac{1}{2}\omega_c$ we have $\ell_o = 0$ and thus

$$L = (1 - f_o(T))\ I_{cl}\ \omega \qquad (42)$$

This is just the phenomenon of NCRI as given by eqn. (28), with the "normal fraction" $f_n(T)$ identified with the "non-condensed fraction" $(1-f_o(T))$. For general ω we expect the $L(\omega)$ relation to be given by the pattern of fig. (3b) (which is drawn for simplicity for the case $T = 0$).



(a) Normal liquid



(b) BEC System (T=0)

FIG. 3: Behavior of a system in the geometry of Fig. (2) when container is rotated with angular frequency ω.
(a) Normal system.
(b) System with BEC at $T = 0$.
(At nonzero $T < T_c$, the horizontal lines are tilted around their centers at an angle $< 45°$.)

It is now easy to see intuitively how the argument will go for the more physically realistic case of an interacting Bose system such as liquid ^4He, or for a Fermi system such as the electrons in metals. Since the "wave function" of the condensate, or equivalently the order parameter (see eqns. (9) and (15)) is essentially nothing more than the Schrödinger wave function of a single particle (or in the Fermi case the center-of-mass wave function of a pair of particles) it must obey the standard "single-valuedness boundary condition" (SVBC); that is, when we take the particle (pair) once around the ring and bring it back to its starting point, the phase of the wave function can have changed only by a multiple of 2π (including of course zero). For a cylindrically uniform geometry this means that the angular dependence of the condensate wave function will be simply of the form

$$\Psi_\ell(\Theta) = \text{const.}\exp\ i\ell\theta \qquad \ell = 0, \pm1,\ \pm2... \qquad (43)$$

where θ is the angle around the annulus as in fig. 2. Thus the single-particle energy is again given by eqn. (35), and if we assume that just as in the noninteracting case the condensate forms in the state with the lowest value of this energy we find that the equilibrium value ℓ_o of ℓ is again given by (40). However, we can no longer necessarily assume that in this state the angular momentum is simply $N_o(T)\hbar\ell_o$, since the condensate may "drag" some of the noncondensed particles with it. If we denote the sum of $N_o(T)$ and the number of "dragged" particles by $Nf_S(T)$, we find (cf. eqn. (41))

$$L = (1 - f_S(T))I_{cl}\omega + f_S(T)I_{cl}\omega_c\ell_o \qquad (44)$$

which agrees with (28) when $\omega < \omega_c$ (cf. (30)). In real-life liquid ^4He, the value of the condensate fraction $N_o/N \equiv f_o$ is believed to be only $\sim 10\%$ at $T = 0$, while by contrast $f_S(T = 0) = 1$. If we know the excitation spectrum of the liquid, then a famous argument originally due to Landau allows us to calculate $f_n(T)$ (thus $f_S(T)$); see QL Chapter 3, Section 6.

Arguments similar to the above can be applied to the case of an electrically charged system: in that case the analog of the condition $\omega < \frac{1}{2}\omega_c$ is

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[28] and has the lowest value of the "transverse" kinetic energy, which is not explicitly considered in the above argument.

that the total magnetic flux through the ring is less than half the "superconducting flux quantum" $h/2e$, and under these conditions the induced current is given by eqn. (31). For more general values of flux, the expression is

$$\boldsymbol{J} = \frac{\wedge(T)}{2\pi R^2}\, Fr\,(\Phi/\Phi_o) \tag{45}$$

where "Fr" denotes the fractional part (i.e. the (algebraic) distance to the nearest integer); evidently this reduces to (31) where $|\Phi/\Phi_o| < 1/2$. For a discussion of the phenomenon of "flux quantization" which is implied by this result, see QL ch 5 section (5.6).

We now turn to the question of metastability of supercurrents. It should be emphasised that (contrary to the impression sometimes given in the literature) the existence of NCRI is *not* a sufficient condition for such metastability; indeed, as we shall see below, the free Bose gas possesses the former property but not the latter. Let us suppose that by the method described above we have set up a persistent current in our examples. According to the above arguments this corresponds to having formed the condensate in the single-particle state with angular momentum quantum number $\ell_o = \text{int.}(\omega/\omega_c - 1/2) \neq 0$ (where ω was the angular velocity of the container as we cooled from the normal phase into the BEC phase). When we stop the container, the normal component comes to rest, but the condensate persists in the state ℓ_o, and since it continues to "drag" some noncondensed particles the total angular momentum is $N f_S(T)\ell_o\hbar$. As we have seen, this angular momentum can be changed reversibly by varying the temperature while always staying below T_λ, which indicates that under this condition the condensate persists indefinitely in the state ℓ_o.

Why can the condensate wave function not evolve from this state ($\chi_o \sim e^{i\ell\theta}$) to the ground state form ($\chi_o \sim$ const.)? After all, an electron in an atom which is initially in an $\ell \neq 0$ state (say a p-state) has no particular difficulty in decaying to the $\ell = 0$ state, and at first sight the problem is similar. Indeed, a free Bose gas would behave in a way similar to the electron, and thus show no metastability of supercurrents. However, let us examine the process involved a little more closely, taking for definiteness the case $\ell_o = 1$ (though in real life it is likely to be $\gg 1$). Suppose we try the ansatz (which would be a good description of the atomic transition in the approximation that the radiation field is described classically):

$$\chi_o(t) = a(t)\psi_p + b(t)\psi_S, \quad |a(t)|^2 + |b(t)|^2 = 1,$$

$$a(-\infty) = b(\infty) = 1 \tag{46}$$

where apart from their common normalization

$$\psi_S = 1, \qquad \psi_p = \exp\ i\theta \tag{47}$$

If we now calculate the density of (condensate) particles, $\rho(\theta)$, as a function of t, we see that

$$\rho(\theta : t) = 1 + 2\ Re\ \left\{a^*(t)b(t)e^{i\theta}\right\} \tag{48}$$

i.e. it is nonuniform in space, and in fact must have a zero at some point on the ring at some intermediate time. Now, for the electron in the atom, and equally for the free Bose gas, the energy is simply (proportional to) the expression

$$E(t) = |a(t)|^2\ E_p + |b(t)|^2 E_S \tag{49}$$

and is uniformly decreasing with $a(t)$; this is a consequence of the linearity of the Schrödinger equation. In the case of an interacting system such as liquid ^4He, however, there is a crucial difference: there is also a term in the (free) energy proportional to $|\chi_o(\boldsymbol{r})|^4$, or equivalently to $|\Psi(\boldsymbol{r})|^4$, with a positive coefficient; cf. eqn. (20). It is easy to verify that in the annular geometry under discussion this term is proportional to the expression

$$\int (\rho(\theta : t))^2 d\,\theta \tag{50}$$

which for a $\rho(\theta : t)$ of the form (48) contains a term $2|a(t)|^2 \cdot |b(t)|^2$. This term is zero in the (spatially uniform) initial and final states, but has a nonzero positive value in intermediate states, reaching a maximum value of 1. Thus, if the coefficient of this term is large enough compared to $E_p - E_s$ (which is almost invariably the case in a realistic geometry for small ℓ_o, except extremely close to T_c) this term provides an *energy barrier* against decay of the circulating-current state; since in practice this energy barrier is very large compared to k_BT, thermal fluctuations cannot overcome it, and the circulating-current state persists indefinitely.

To put it in a formally different but equivalent way, the "winding number" ℓ is a *topological invariant*; it is impossible to go continuously in an annulus from the state $\ell = \ell_o (\neq 0)$ to the state $\ell = 0$ without depressing the amplitude of the condensate wave to zero for some value[29] of θ, and as

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[29] This argument implicitly assumes that χ_o (or Ψ) is constant over any plane of constant θ. If we relax this assumption, further possibilities arise but the energy barrier is still large: see QL Chapter 3, Section 5.

indicated this costs a large amount of energy. However, it is crucial to note that this argument only works because the order parameter we are considering is, as in superfluid ^4He, a complex scalar quantity. For more sophisticated forms of order parameter, such as that believed to characterize the orbital states of ^3He-A, the topological argument is no longer valid: it turns out that it is possible to change the winding member by multiples of 2 without introducing any nodes, indeed while maintaining its *amplitude* at the original value everywhere. Thus in an ideal world, where one could neglect the primary effects of boundaries etc., while the $\ell = \pm 1$ states of $^3He - A$ in an annular geometry would be "marginally" metastable, all other $\ell \neq 0$ states would be unstable against decay: see e.g. QL section 6.5. This shows rather dramatically that "broken symmetry" by itself cannot explain all the phenomena of superfluidity.

5. Conclusion

The basic message of this paper has been that the occurrence of quantum condensation is a *sufficient* condition to explain most of the anomalous properties of superfluid systems, although in some cases, such as the metastability of supercurrents, it needs to be supplemented with other considerations such as the topological properties of the condensate wave function. It is a different, and very interesting, question whether quantum condensation is a *necessary* condition for all or some of these phenomena to occur; existing theoretical results on two- and one-dimensional systems tend to indicate that it is not, and some further intriguing possibilities are raised by recent experiments which suggest the occurrence of NCRI in *solid* ^4He: see QL Chapter 8, Section 3. Unfortunately there is no space to discuss these questions here.

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