

## Chapter 8

# Identical Particles

Until now, most of our focus has been on the quantum mechanical behaviour of *individual* particles, or problems which can be “factorized” into independent single-particle systems.<sup>1</sup> However, most physical systems of interest involve the interaction of large numbers of particles; electrons in a solid, atoms in a gas, etc. In classical mechanics, particles are always distinguishable in the sense that, at least formally, their “trajectories” through phase space can be traced and their identity disclosed. However, in quantum mechanics, the intrinsic uncertainty in position, embodied in Heisenberg’s principle, demands a careful and separate consideration of distinguishable and indistinguishable particles. In the present section, we will consider how to formulate the wavefunction of many-particle systems, and address some of the (sometimes striking and often counter-intuitive) implications of particle indistinguishability.

### 8.1 Quantum statistics

Consider then two identical particles confined to a box in one-dimension. Here, by identical, we mean that the particles can not be discriminated by some internal quantum number. For example, we might have two electrons of the same spin. The normalized two-particle wavefunction  $\psi(x_1, x_2)$ , which gives the probability  $|\psi(x_1, x_2)|^2 dx_1 dx_2$  of finding simultaneously one particle in the interval  $x_1$  to  $x_1 + dx_1$  and another between  $x_2$  to  $x_2 + dx_2$ , only makes sense if  $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$ , since we can’t know which of the two indistinguishable particles we are finding where. It follows from this that the wavefunction can exhibit two (and, generically, only two) possible symmetries under exchange:  $\psi(x_1, x_2) = \psi(x_2, x_1)$  or  $\psi(x_1, x_2) = -\psi(x_2, x_1)$ .<sup>2</sup> If two identical particles have a symmetric wavefunction in some state, particles of that type always have symmetric wavefunctions, and are called **bosons**. (If in some other state they had an antisymmetric wavefunction, then a linear

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<sup>1</sup>For example, our treatment of the hydrogen atom involved the separation of the system into centre of mass and relative motion. Each could be referred to an effective single-particle dynamics.

<sup>2</sup>We could in principle have  $\psi(x_1, x_2) = e^{i\alpha}\psi(x_2, x_1)$ , with  $\alpha$  a constant phase. However, in this case we would not recover the original wavefunction on exchanging the particles twice. Curiously, in some two-dimensional theories used to describe the fractional quantum Hall effect, there exist collective excitations of the electron system — called **anyons** — that do have this kind of property. For a discussion of this point, one may refer to the seminal paper of J. M. Leinaas and J. Myrheim, *On the theory of identical particles*. *Il Nuovo Cimento B***37**, 1-23 (1977). Such anyonic systems have been proposed as a strong candidate for the realization of quantum computation. For a pedagogical discussion, we refer to an entertaining discussion by C. Nayak, S. H. Simon, A. Stern, M. Freedman, S. Das Sarma, *Non-Abelian Anyons and Topological Quantum Computation*, *Rev. Mod. Phys.* **80**, 1083 (2008). However, all ordinary “fundamental” particles are either bosons or fermions.

superposition of those states would be neither symmetric nor antisymmetric, and so could not satisfy the relation  $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$ .) Similarly, particles having antisymmetric wavefunctions are called **fermions**.

To construct wavefunctions for three or more fermions, let first suppose that the particles do not interact with each other, and are confined by a spin-independent potential, such as the Coulomb field of a nucleus. In this case, the Hamiltonian will be symmetric in the fermion degrees of freedom,

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m} + \frac{\hat{\mathbf{p}}_2^2}{2m} + \frac{\hat{\mathbf{p}}_3^2}{2m} \cdots + V(\mathbf{r}_1) + V(\mathbf{r}_2) + V(\mathbf{r}_3) + \cdots,$$

and the solutions of the Schrödinger equation will be products of eigenfunctions of the single-particle Hamiltonian  $\hat{H}_s = \hat{\mathbf{p}}^2/2m + V(\mathbf{r})$ . However, single products such as  $\psi_a(1)\psi_b(2)\psi_c(3)$  do not have the required antisymmetry property under the exchange of any two particles. (Here  $a, b, c, \dots$  label the single-particle eigenstates of  $\hat{H}_s$ , and  $1, 2, 3, \dots$  denote *both* space and spin coordinates of single particles, i.e.  $1$  stands for  $(\mathbf{r}_1, s_1)$ , etc.)

We could achieve the necessary antisymmetrization for particles  $1$  and  $2$  by subtracting the same product wavefunction with the particles  $1$  and  $2$  interchanged, i.e.  $\psi_a(1)\psi_b(2)\psi_c(3) \mapsto (\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))\psi_c(3)$ , ignoring the overall normalization for now. However, the wavefunction needs to be antisymmetrized with respect to *all* possible particle exchanges. So, for  $3$  particles, we must add together all  $3!$  permutations of  $1, 2, 3$  in the state  $a, b, c$ , with a factor  $-1$  for each particle exchange necessary to get to a particular ordering from the original ordering of  $1$  in  $a$ ,  $2$  in  $b$ , and  $3$  in  $c$ . In fact, such a sum over permutations is precisely the *definition* of the determinant. So, with the appropriate normalization factor:

$$\psi_{abc}(1, 2, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(1) & \psi_b(1) & \psi_c(1) \\ \psi_a(2) & \psi_b(2) & \psi_c(2) \\ \psi_a(3) & \psi_b(3) & \psi_c(3) \end{vmatrix}.$$

The determinantal form makes clear the antisymmetry of the wavefunction with respect to exchanging any two of the particles, since exchanging two rows of a determinant multiplies it by  $-1$ . We also see from the determinantal form that the three states  $a, b, c$  *must* all be different, for otherwise two columns would be identical, and the determinant would be zero. This is just the manifestation of Pauli's exclusion principle: no two fermions can be in the same state.

Although these determinantal wavefunctions (known as **Slater determinants**), involving superpositions of single-particle states, are only strictly correct for non-interacting fermions, they provide a useful platform to describe electrons in atoms (or in a metal), with the electron-electron repulsion approximated by a single-particle potential. For example, the Coulomb field in an atom, as seen by the outer electrons, is partially shielded by the inner electrons, and a suitable  $V(\mathbf{r})$  can be constructed self-consistently, by computing the single-particle eigenstates and finding their associated charge densities (see section 9.2.1).

In the bosonic system, the corresponding many-particle wavefunction must be symmetric under particle exchange. We can obtain such a state by expanding all of the contributing terms from the Slater determinant and setting all of the signs to be positive. In other words, the bosonic wave function describes the uniform (equal phase) superposition of all possible permutations of product states.

## 8.2 Space and spin wavefunctions

Although the methodology for constructing a basis of many-particle states outlined above is generic, it is not particularly convenient when the Hamiltonian is spin-independent. In this case we can simplify the structure of the wavefunction by factorizing the spin and spatial components. Suppose we have two electrons (i.e. fermions) in some spin-independent potential  $V(\mathbf{r})$ . We know that the two-electron wavefunction must be antisymmetric under particle exchange. Since the Hamiltonian has no spin-dependence, we must be able to construct a set of common eigenstates of the Hamiltonian, the total spin, and the  $z$ -component of the total spin. For two electrons, there are four basis states in the spin space, the  $S = 0$  spin singlet state,  $|\chi_{S=0, S_z=0}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle)$ , and the three  $S = 1$  spin triplet states,

$$|\chi_{11}\rangle = |\uparrow_1\uparrow_2\rangle, \quad |\chi_{10}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle), \quad |\chi_{1,-1}\rangle = |\downarrow_1\downarrow_2\rangle.$$

Here the first arrow in the ket refers to the spin of particle 1, the second to particle 2.

▷ EXERCISE. By way of revision, it is helpful to recapitulate the discussion of the addition of spin  $s = 1/2$  angular momenta. By setting  $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ ,<sup>3</sup> where  $\mathbf{S}_1$  and  $\mathbf{S}_2$  are two spin  $1/2$  degrees of freedom, construct the matrix elements of the total spin operator  $\mathbf{S}^2$  for the four basis states,  $|\uparrow\uparrow\rangle$ ,  $|\uparrow\downarrow\rangle$ ,  $|\downarrow\uparrow\rangle$ , and  $|\downarrow\downarrow\rangle$ . From the matrix representation of  $\mathbf{S}^2$ , determine the four eigenstates. Show that one corresponds to a total spin zero state and three correspond to spin 1.

Hint: begin by proving that, for two spin  $s = 1/2$  degree of freedom,  $\mathbf{S}^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 = 2 \times s(s+1)\hbar^2 + 2S_1^z S_2^z + S_1^+ S_2^- + S_1^- S_2^+$ .

It is evident that the spin singlet wavefunction is antisymmetric under the exchange of two particles, while the spin triplet wavefunction is symmetric. For a general state, the total wavefunction for the two electrons in a common eigenstate of  $\mathbf{S}^2$ ,  $S_z$  and the Hamiltonian  $\hat{H}$  then has the form:

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(s_1, s_2),$$

where  $\chi(s_1, s_2) = \langle s_1, s_2 | \chi \rangle$ . For two electron degrees of freedom, the total wavefunction,  $\Psi$ , must be antisymmetric under exchange. It follows that a pair of electrons in the spin *singlet* state must have a *symmetric* spatial wavefunction,  $\psi(\mathbf{r}_1, \mathbf{r}_2)$ , whereas electrons in the spin *triplet* states must have an *antisymmetric* spatial wavefunction. Before discussing the physical consequences of this symmetry, let us mention how this scheme generalizes to more particles.

▷ INFO. **Symmetry of three-electron wavefunctions:** Unfortunately, in seeking a factorization of the Slater determinant into a product of spin and spatial components for three electrons, things become more challenging. There are now  $2^3 = 8$  basis states in the spin space. Four of these are accounted for by the spin  $3/2$  state with  $S_z = 3/2, 1/2, -1/2, -3/2$ . Since all spins are aligned, this is evidently a symmetric state, so must be multiplied by an antisymmetric spatial wavefunction, itself a determinant. So far so good. But the other four states involve two pairs of total spin  $1/2$  states built up of a singlet and an unpaired spin. They are orthogonal to the symmetric spin  $3/2$  state, so they can't be symmetric. But they can't be antisymmetric either, since in each such state, two of the spins must be pointing in the same direction! An example of such a state is presented by  $|\chi\rangle = |\uparrow_1\rangle \otimes \frac{1}{\sqrt{2}}(|\uparrow_2\downarrow_3\rangle - |\downarrow_2\uparrow_3\rangle)$ . Evidently, this must be multiplied by a spatial wavefunction

<sup>3</sup>Here, for simplicity, we have chosen not to include hats on the spin angular momentum operators.

symmetric in 2 and 3. But to recover a total wave function with *overall* antisymmetry it is necessary to add more terms:

$$\Psi(1, 2, 3) = \chi(s_1, s_2, s_3)\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \chi(s_2, s_3, s_1)\psi(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1) + \chi(s_3, s_1, s_2)\psi(\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2).$$

Requiring the spatial wavefunction  $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  to be symmetric in 2, 3 is sufficient to guarantee the overall antisymmetry of the total wavefunction  $\Psi$ .<sup>4</sup> For more than three electrons, similar considerations hold. The mixed symmetries of the spatial wavefunctions and the spin wavefunctions which together make a totally antisymmetric wavefunction are quite complex, and are described by **Young diagrams (or tableaux)**.<sup>5</sup> A discussion of this scheme reaches beyond the scope of these lectures.

▷ EXERCISE. A hydrogen atom consists of two fermions, the proton and the electron. By considering the wavefunction of two non-interacting hydrogen atoms under exchange, show that the atom transforms as a boson. In general, if the number of fermions in a composite particle is odd, then it is a fermion, while if even it is a boson. Quarks are fermions: baryons consist of three quarks and so translate to fermions while mesons consist of two quarks and translate to bosons.

### 8.3 Physical consequences of particle statistics

The overall antisymmetry demanded by the many-fermion wavefunction has important physical implications. In particular, it determines the magnetic properties of atoms. The magnetic moment of the electron is aligned with its spin, and even though the spin variables do not appear in the Hamiltonian, the energy of the eigenstates depends on the relative spin orientation. This arises from the electrostatic repulsion between electrons. In the spatially antisymmetric state, the probability of electrons coinciding at the same position necessarily vanishes. Moreover, the nodal structure demanded by the antisymmetry places the electrons further apart on average than in the spatially symmetric state. Therefore, the electrostatic repulsion raises the energy of the spatially symmetric state above that of the spatially antisymmetric state. It therefore follows that the lower energy state has the electron spins pointing in the same direction. This argument is still valid for more than two electrons, and leads to **Hund's rule** for the magnetization of incompletely filled inner shells of electrons in transition metal and rare earths atoms (see chapter 9). This is the first step in understanding ferromagnetism.

A gas of hydrogen molecules provides another manifestation of wavefunction antisymmetry. In particular, the specific heat depends sensitively on whether the two protons (spin 1/2) in  $H_2$  have their spins parallel or antiparallel, even though that alignment involves only a very tiny interaction energy. If the proton spins occupy a spin singlet configuration, the molecule is called **parahydrogen** while the triplet states are called **ortho-hydrogen**. These two distinct gases are remarkably stable - in the absence of magnetic impurities, paraortho transitions take weeks.

The actual energy of interaction of the proton spins is of course completely negligible in the specific heat. The important contributions to the specific heat

<sup>4</sup>Particle physics enthusiasts might be interested to note that functions exactly like this arise in constructing the spin/flavour wavefunction for the proton in the quark model (Griffiths, Introduction to Elementary Particles, page 179).

<sup>5</sup>For a simple introduction, see Sakurai's textbook (section 6.5) or chapter 63 of the text on quantum mechanics by Landau and Lifshitz.

are the usual kinetic energy term, and the rotational energy of the molecule. This is where the overall (space  $\times$  spin) antisymmetric wavefunction for the protons plays a role. Recall that the parity of a state with rotational angular momentum  $\ell$  is  $(-1)^\ell$ . Therefore, parahydrogen, with an antisymmetric proton spin wavefunction, must have a symmetric proton *spatial* wavefunction, and so can only have even values of the rotational angular momentum. Orthohydrogen can only have odd values. The energy of the rotational level with angular momentum  $\ell$  is  $E_\ell^{\text{rot}} = \hbar^2 \ell(\ell + 1)/I$ , where  $I$  denotes the moment of inertia of the molecule. So the two kinds of hydrogen gas have different sets of rotational energy levels, and consequently different specific heats.

▷ EXERCISE. Determine the degeneracy of ortho- and parahydrogen. By expressing the state occupancy of the rotational states through the Boltzmann factor, determine the low temperature variation of the specific heat for the two species.

▷ EXAMPLE: As a final example, and one that will feed into our discussion of multielectron atoms in the next chapter, let us consider the implications of particle statistics for the **excited state spectrum of Helium**. After Hydrogen, Helium is the simplest atom having two protons and two neutrons in the nucleus ( $Z = 2$ ), and two bound electrons. As a complex many-body system, we have seen already that the Schrödinger equation is analytically intractable and must be treated perturbatively. Previously, in chapter 7, we have used the ground state properties of Helium as a vehicle to practice perturbation theory. In the absence of direct electron-electron interaction, the Hamiltonian

$$\hat{H}_0 = \sum_{n=1}^2 \left[ \frac{\hat{\mathbf{p}}_n^2}{2m} + V(\mathbf{r}_n) \right], \quad V(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r},$$

is separable and the wavefunction can be expressed through the states of the hydrogen atom,  $\psi_{n\ell m}$ . In this approximation, the ground state wavefunction involves both electrons occupying the  $1s$  state leading to an antisymmetric spin singlet wavefunction for the spin degrees of freedom,  $|\Psi_{\text{g.s.}}\rangle = (|100\rangle \otimes |100\rangle) \otimes |\chi_{00}\rangle$ . In chapter 7, we made use of both the perturbative series expansion and the variational method to determine how the ground state energy is perturbed by the repulsive electron-electron interaction,

$$\hat{H}_1 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Now let us consider the implications of particle statistics on the spectrum of the lowest excited states.

From the symmetry perspective, the ground state wavefunction belongs to the class of states with symmetric spatial wavefunctions, and antisymmetric spin (singlet) wavefunctions. These states are known as **parahelium**. In the absence of electron-electron interaction, the first excited states are degenerate and have the form,

$$|\psi_{\text{p}}\rangle = \frac{1}{\sqrt{2}} (|100\rangle \otimes |2\ell m\rangle + |2\ell m\rangle \otimes |100\rangle) \otimes |\chi_{00}\rangle.$$

The second class of states involve an antisymmetric spatial wavefunction, and symmetric (triplet) spin wavefunction. These states are known as **orthohelium**. Once again, in the absence of electron-electron interaction, the first excited states are degenerate and have the form,

$$|\psi_{\text{o}}\rangle = \frac{1}{\sqrt{2}} (|100\rangle \otimes |2\ell m\rangle - |2\ell m\rangle \otimes |100\rangle) \otimes |\chi_{1s_z}\rangle.$$

The perturbative shift in the ground state energy has already been calculated within the framework of first order perturbation theory. Let us now consider the shift

in the excited states. Despite the degeneracy, since the off-diagonal matrix elements vanish, we can make use of the first order of perturbation theory to compute the shift. In doing so, we obtain

$$\Delta E_{nl}^{p,o} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 |\psi_{100}(\mathbf{r}_1)\psi_{n\ell 0}(\mathbf{r}_2) \pm \psi_{n\ell 0}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

with the plus sign refers to parahelium and the minus to orthohelium. Since the matrix element is independent of  $m$ , the  $m = 0$  value considered here applies to all values of  $m$ . Rearranging this equation, we thus obtain  $\Delta E_{nl}^{p,o} = J_{nl} \pm K_{nl}$  where

$$J_{nl} = \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{|\psi_{100}(\mathbf{r}_1)|^2 |\psi_{n\ell 0}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$K_{nl} = \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{\psi_{100}^*(\mathbf{r}_1)\psi_{n\ell 0}^*(\mathbf{r}_2)\psi_{100}(\mathbf{r}_2)\psi_{n\ell 0}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Physically, the term  $J_{nl}$  represents the electrostatic interaction energy associated with the two charge distributions  $|\psi_{100}(\mathbf{r}_1)|^2$  and  $|\psi_{n\ell 0}(\mathbf{r}_2)|^2$ , and it is clearly positive. By contrast, the **exchange term**, which derives from the antisymmetry of the wavefunction, leads to a shift with opposite signs for ortho and para states. In fact, one may show that, in the present case,  $K_{nl}$  is positive leading to a positive energy shift for parahelium and a negative shift for orthohelium. Moreover, noting that

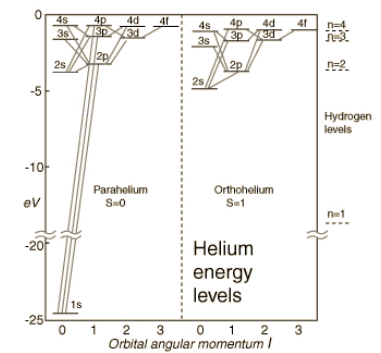
$$2\mathbf{S}_1 \cdot \mathbf{S}_2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2 = \hbar^2 \left( S(S+1) - 2 \times \frac{3}{4} \right) = \hbar^2 \begin{cases} 1/2 & \text{triplet} \\ -3/2 & \text{singlet} \end{cases}$$

the energy shift can be written as

$$\Delta E_{nl}^{p,o} = J_{nl} - \frac{1}{2} \left( 1 + \frac{4}{\hbar^2} \mathbf{S}_1 \cdot \mathbf{S}_2 \right) K_{nl}.$$

This result shows that the electron-electron interaction leads to an effective **ferromagnetic** interaction between spins – i.e. the spins want to be aligned.<sup>6</sup>

In addition to the large energy shift between the singlet and triplet states, electric dipole decay selection rules  $\Delta\ell = \pm 1$ ,  $\Delta s = 0$  (whose origin is discussed later in the course) cause decays from triplet to singlet states (or vice-versa) to be suppressed by a large factor (compared to decays from singlet to singlet or from triplet to triplet). This caused early researchers to think that there were two separate kinds of Helium. The diagrams (right) shows the levels for parahelium (singlet) and for orthohelium (triplet) along with the dominant decay modes.



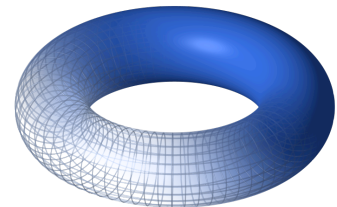
Energy level diagram for ortho- and parahelium showing the first order shift in energies due to the Coulomb repulsion of electrons. Here we assume that one of the electrons stays close to the ground state of the unperturbed Hamiltonian.

## 8.4 Ideal quantum gases

An important and recurring example of a many-body system is provided by the problem of free (i.e. non-interacting) non-relativistic quantum particles in a closed system – a box. The many-body Hamiltonian is then given simply by

$$\hat{H}_0 = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m},$$

where  $\hat{\mathbf{p}}_i = -i\hbar\nabla_i$  and  $m$  denotes the particle mass. If we take the dimensions of the box to be  $L^d$ , and the boundary conditions to be periodic<sup>7</sup> (i.e. the box



<sup>6</sup>A similar phenomenology extends to the interacting metallic system where the exchange interaction leads to the phenomenon of itinerant (i.e. mobile) ferromagnetism – Stoner ferromagnetism.

<sup>7</sup>It may seem odd to consider such an unphysical geometry – in reality, we are invariably dealing with a closed system in which the boundary conditions translate to “hard walls” – think of electrons in a metallic sample. Here, we have taken the boundary conditions to be periodic since it leads to a slightly more simple mathematical formulation. We could equally well consider closed boundary conditions, but we would have to separately discriminate between “even and odd” states and sum them accordingly. Ultimately, we would arrive to the same qualitative conclusions!

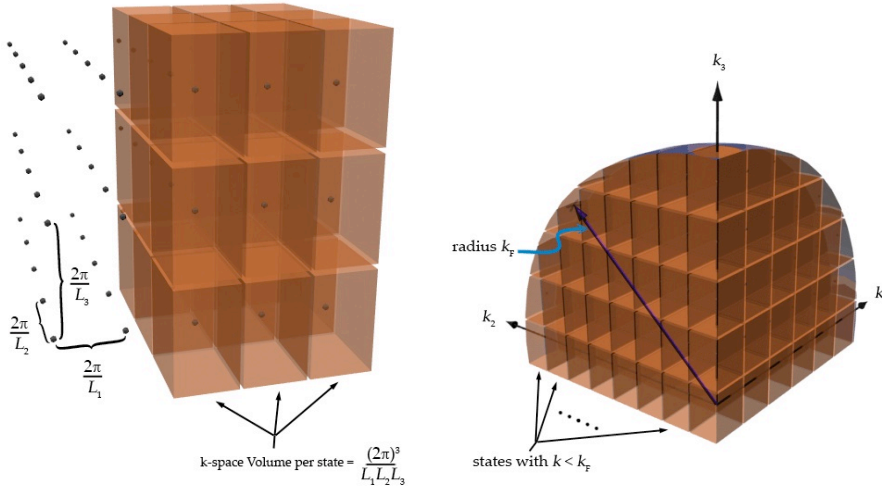


Figure 8.1: (Left) Schematic showing the phase space volume associated with each plane wave state in a Fermi gas. (Right) Schematic showing the state occupancy of a filled Fermi sea.

has the geometry of a  $d$ -torus) the normalised eigenstates of the single-particle Hamiltonian are simply given by plane waves,  $\phi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{L^{d/2}} e^{i\mathbf{k} \cdot \mathbf{r}}$ , with wavevectors taking discrete values,<sup>8</sup>

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, \dots, n_d), \quad n_i \text{ integer.}$$

To address the quantum mechanics of the system, we start with fermions.

### 8.4.1 Non-interacting Fermi gas

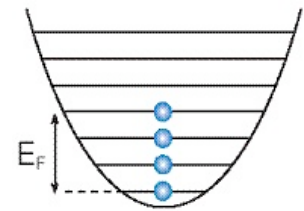
In the (**spinless**) **Fermi system**, Pauli exclusion inhibits the multiple occupancy of single-particle states. In this case, the many-body ground state wavefunction is obtained by filling states sequentially up to the **Fermi energy**,  $E_F = \hbar^2 k_F^2 / 2m$ , where the **Fermi wavevector**,  $k_F$ , is fixed by the number of particles. All the plane wave states  $\phi_{\mathbf{k}}$  with energies lower than  $E_F$  are filled, while all states with energies larger than  $E_F$  remain empty. Since each state is associated with a  $k$ -space volume  $(2\pi/L)^d$  (see Fig. 8.1), in the three-dimensional system, the total number of occupied states is given by  $N = (\frac{L}{2\pi})^3 \frac{4}{3} \pi k_F^3$ , i.e. defining the particle density  $n = N/L^3 = k_F^3 / 6\pi^2$ ,

$$E_F = \frac{\hbar^2}{2m} (6\pi^2 n)^{2/3}.$$

The **density of states** per unit volume,

$$g(E) = \frac{1}{L^3} \frac{dN}{dE} = \frac{1}{6\pi^2} \frac{d}{dE} \left( \frac{2mE}{\hbar^2} \right)^{3/2} = \frac{1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}.$$

▷ EXERCISE. Obtain an expression for the density of states,  $g(E)$  in dimension  $d$ . In particular, show that the density of states varies as  $g(E) \sim E^{(d-2)/2}$ .



Note that the volume of a  $d$ -dimensional sphere is given by  $S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$ .

<sup>8</sup>The quantization condition follows from the periodic boundary condition,  $\phi[\mathbf{r} + L(m_x \hat{\mathbf{x}} + m_y \hat{\mathbf{y}} + m_z \hat{\mathbf{z}})] = \phi(\mathbf{r})$ , where  $\mathbf{m} = (m_x, m_y, m_z)$  denotes an arbitrary vector of integers.

We can also integrate to obtain the total energy density of all the fermions,

$$\frac{E_{\text{tot}}}{L^3} = \frac{1}{L^3} \int_0^{k_F} \frac{4\pi k^2 dk}{(2\pi/L)^3} \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{20\pi^2 m} (6\pi^2 n)^{5/3} = \frac{3}{5} n E_F.$$

▷ INFO. **Degeneracy pressure:** The pressure exerted by fermions squeezed into a small box is what keeps cold stars from collapsing. A **White dwarf** is a remnant of a normal star which has exhausted its fuel fusing light elements into heavier ones (mostly  $^{56}\text{Fe}$ ). As the star cools, it shrinks in size until it is arrested by the degeneracy pressure of the electrons. If the white dwarf acquires more mass, the Fermi energy  $E_F$  rises until electrons and protons abruptly combine to form neutrons and neutrinos, an event known as a supernova. The **neutron star** left behind is supported by degeneracy pressure of the neutrons.

We can compute the degeneracy pressure from analyzing the dependence of the energy on volume for a fixed number of particles (fermions). From thermodynamics, we have  $dE = \mathbf{F} \cdot d\mathbf{s} = PdV$ , i.e. the pressure  $P = -\partial_V E_{\text{tot}}$ . The expression for  $E_{\text{tot}}$  given above shows that the pressure depends on the volume and particle number  $N$  only through the density,  $n$ . To determine the point of collapse of stars, we must compare this to the pressure exerted by gravity. We can compute this approximately, ignoring general relativity and, more significantly, the variation of gravitational pressure with radius. The mass contained within a shell of width  $dr$  at radius  $r$  is given by  $dm = 4\pi\rho r^2 dr$ , where  $\rho$  denotes the density. This mass experiences a gravitational force from the mass contained within the shell,  $M = \frac{4}{3}\pi r^3 \rho$ . The resulting potential energy is given by

$$E_G = - \int \frac{GMdm}{r} = - \int_0^R d^3r \frac{G(\frac{4}{3}\pi r^3 \rho)4\pi r^2 \rho}{r} = - \frac{(4\pi)^2}{15} G\rho^2 R^5 = - \frac{3GM^2}{5R},$$

The mass of the star is dominated by nucleons,  $M = NM_N$ , where  $M_N$  denotes the nucleon mass and  $N$  their number. Substituting this expression into the formula for the energy, we find  $E_G = -\frac{3}{5}G(NM_N)^2(\frac{4\pi}{3V})^{\frac{1}{3}}$ , from which we obtain the pressure,

$$P_G = -\partial_V E_G = -\frac{1}{5}G(NM_N)^2 \left(\frac{4\pi}{3}\right)^{1/3} V^{-4/3}.$$

For the point of instability, this pressure must perfectly balance with the degeneracy pressure. For a white dwarf, the degeneracy pressure is associated with electrons and given by,

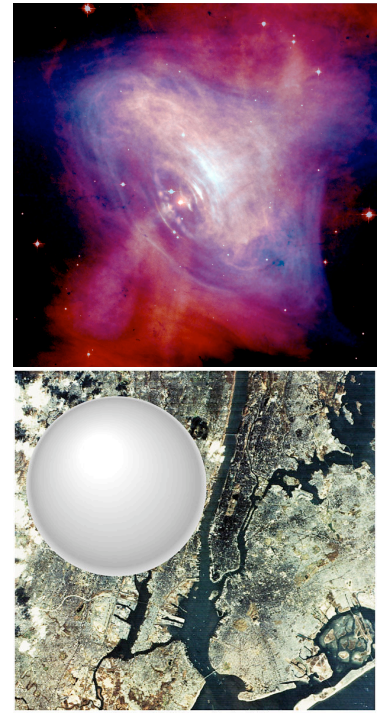
$$P_e = -\partial_V E_{\text{tot}} = \frac{\hbar^2}{60\pi^2 m_e} (6\pi^2 N_e)^{5/3} V^{-5/3}.$$

Comparing  $P_G$  and  $P_e$ , we can infer the critical radius,

$$R \approx \frac{\hbar^2 N_e^{5/3}}{Gm_e M_N^2 N^2}.$$

Since there are about two nucleons per electron,  $N_N \approx 2N_e$ ,  $R \simeq \frac{\hbar^2}{Gm_e M_N^2} N^{-\frac{1}{3}}$ , showing that radius *decreases* as we add mass. For one solar mass,  $N = 10^{57}$ , we get a radius of ca. 7200 km, the size of the Earth while  $E_F \simeq 0.2$  MeV.

During the cooling period, a white dwarf star will shrink in size approaching the critical radius. Since the pressure from electron degeneracy grows faster than the pressure of gravity, the star will stay at about Earth size even when it cools. If the star is more massive, the Fermi energy goes up and it becomes possible to absorb the electrons into the nucleons, converting protons into neutrons. If the electrons disappear this way, the star collapses suddenly down to a size for which the Fermi pressure of the neutrons stops the collapse. Some white dwarfs stay at Earth size for a long time as they suck in mass from their surroundings. When they have just enough mass, they collapse forming a neutron star and making a supernova. The supernovae are all nearly identical since the dwarfs are gaining mass very slowly. The brightness



The image shows the crab pulsar, a magnetized neutron star spinning at 30 times per second, that resides at the centre of the crab nebula. The pulsar powers the X-ray and optical emission from the nebula, accelerating charged particles and producing the glowing X-ray jets. Ring-like structures are X-ray emitting regions where the high energy particles slam into the nebular material. The innermost ring is about a light-year across. With more mass than the Sun and the density of an atomic nucleus; the spinning pulsar is the collapsed core of a massive star that exploded, while the nebula is the expanding remnant of the star's outer layers. The supernova explosion was witnessed in the year 1054. The lower image shows the typical size of a neutron star against Manhattan!



of this type of supernova has been used to measure the accelerating expansion of the universe. An estimate the neutron star radius using the formulae above leads to

$$\frac{R_{\text{neutron}}}{R_{\text{white dwarf}}} \simeq \frac{m_e}{M_N} \simeq 10^{-3},$$

i.e. ca. 10 km. If the pressure at the center of a neutron star becomes too great, it collapses to become a black hole.

### 8.4.2 Ideal Bose gas

In a system of  $N$  spinless **non-interacting bosons**, the ground state of the many-body system is described simply by a wavefunction in which all  $N$  particles occupy the lowest energy single-particle state, i.e. in this case, the fully symmetrized wavefunction can be expressed as the product state,  $\psi_B(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \phi_{\mathbf{k}=0}(\mathbf{r}_i)$ . (More generally, for a confining potential  $V(\mathbf{r})$ ,  $\phi_{\mathbf{k}}(\mathbf{r})$  denote the corresponding single-particle bound states with  $\mathbf{k}$  the associated quantum numbers.) However, in contrast to the Fermi system, the transit to the ground state from non-zero temperatures has an interesting feature with intriguing experimental ramifications. To understand why, let us address the thermodynamics of the system.

For independent bosons, the number of particles in plane wave state  $\mathbf{k}$  with energy  $\epsilon_{\mathbf{k}}$  is given by the **Bose-Einstein distribution**,

$$n_{\mathbf{k}} = \frac{1}{e^{(\epsilon_{\mathbf{k}} - \mu)/k_B T} - 1},$$

where the chemical potential,  $\mu$ , is fixed by the condition  $N = \sum_{\mathbf{k}} n_{\mathbf{k}}$  with  $N$  the total number of particles. In a three-dimensional system, for  $N$  large, we may approximate the sum by an integral over momentum space setting  $\sum_{\mathbf{k}} \mapsto (\frac{L}{2\pi})^3 \int d^3k$ . As a result, we find that

$$\frac{N}{L^3} = n = \frac{1}{(2\pi)^3} \int d^3k \frac{1}{e^{(\epsilon_{\mathbf{k}} - \mu)/k_B T} - 1}.$$

For a free particle system, where  $\epsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m}$ , this means that

$$n = \frac{1}{\lambda_T^3} \text{Li}_{3/2}(\mu/k_B T), \quad (8.1)$$

where  $\text{Li}_n(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^n}$  denotes the polylogarithm, and  $\lambda_T = (\frac{\hbar^2}{2\pi m k_B T})^{1/2}$  denotes the thermal wavelength, i.e. the length scale at which the corresponding energy scale becomes comparable to temperature. As the density of particles increase, or the temperature falls,  $\mu$  increases from negative values until, at some critical value of density,  $n_c = \lambda_T^{-3} \zeta(3/2)$ ,  $\mu$  becomes zero (note that  $\text{Li}_n(0) = \zeta(n)$ ). Equivalently, inverting, this occurs at a temperature,

$$k_B T_c = \alpha \frac{\hbar^2}{m} n^{2/3}, \quad \alpha = \frac{2\pi}{\zeta^{2/3}(3/2)}.$$

Clearly, since  $n_{\mathbf{k}} \geq 0$ , the Bose distribution only makes sense for  $\mu$  negative. So what happens at this point?

Consider first what happens at zero temperature. Since the particles are bosons, the ground state consists of every particle sitting in the lowest energy

#### Satyendra Nath Bose 1894–1974

An Indian physicist who is best known for his work on quantum mechanics in the early 1920s, providing the foundation for Bose-Einstein statistics and the development of the theory of the Bose-Einstein condensate. He is honored as the namesake of the boson.



state ( $\mathbf{k} = 0$ ). But such a singular distribution was excluded by the replacement of the sum by the integral. Suppose that, at  $T < T_c$ , we have a thermodynamic fraction  $f(T)$  of particles sitting in this state.<sup>9</sup> Then the chemical potential may stay equal to zero and Eq. (8.1) becomes  $n = \frac{1}{\lambda_T^3} \zeta(3/2) + f(T)n$ , where  $f(T)$  denotes the fraction of particles in the ground state. But, since  $n = \frac{1}{\lambda_{T_c}^3} \zeta(3/2)$ , we have

$$f(T) = 1 - \left( \frac{\lambda_{T_c}}{\lambda_T} \right)^3 = 1 - \left( \frac{T}{T_c} \right)^{3/2}.$$

The unusual, highly quantum degenerate state emerging below  $T_c$  is known as a **Bose-Einstein condensate (BEC)**.<sup>10</sup>

▷ EXERCISE. **Ideal Bose gas in a harmonic trap:** Show that, in an harmonic trap,  $V(\mathbf{r}) = \frac{1}{2}m\omega^2\mathbf{r}^2$ , the corresponding relation is given by  $f(T) = N[1 - (\frac{T}{T_{\text{BEC}}})^3]$ , with  $k_{\text{B}}T_c = \hbar\omega(N/\zeta(3))^{1/3}$ .

▷ INFO. Although solid state systems continue to provide the most “accessible” arena in which to study the properties of quantum liquids and gases, in recent years, a new platform has been realized through developments in atomic physics – in the field of **ultracold atom physics**, dilute atomic vapours are maintained at temperatures close to absolute zero, typically below some tenths of microkelvins, where their behaviour are influenced by the effects of quantum degeneracy. The method of cooling the gas has a long history which it would be unwise to detail here. But in short, alkali atoms can be cooled by a technique known as **laser cooling**. Laser beams, in addition to carrying heat, also carry momentum. As a result, photons impart a pressure when they collide with atoms. The acceleration of an atom due to photons can be some four orders of magnitude larger than gravity. Consider then a geometry in which atoms are placed inside two counterpropagating laser beams. To slow down, an atom has to absorb a photon coming towards it, and not from behind. This can be arranged by use of the Doppler shift. By tuning the laser frequency a little bit towards the low-frequency (“red”) side of a resonance, the laser beam opposing the atom is Doppler shifted to a higher (more “blue”) frequency. Thus the atom is more likely to absorb that photon. A photon coming from behind the atom is now a little bit redder, which means the atom is less likely to absorb that photon. So in whichever direction the atom is moving, the laser beam opposing the motion seems stronger to the atom, and it slows the atom down. If you multiply this by three and have laser beams coming from the north, south, east, west, up, and down, you get an “**optical molasse**”. If you walk around in a pot full of molasses, whichever direction you go, the molasses somehow knows that is the direction to push against. It’s the same idea.

In the study of ultracold atomic gases, experimentalists are usually concerned with addressing the properties of neutral alkali atoms. The number of atoms in a typical experiment ranges from  $10^4$  to  $10^7$ . The atoms are coned in a trapping potential of magnetic or optical origin, with peak densities at the centre of the trap ranging from  $10^{13}$   $\text{cm}^{-3}$  to  $10^{15}$   $\text{cm}^{-3}$ . The development of quantum phenomena such as Bose-Einstein condensation requires a phase-space density of order unity, or  $n\lambda_T^3 \sim 1$  where  $\lambda_T$  denotes the thermal de Broglie wavelength. These densities correspond to temperatures,

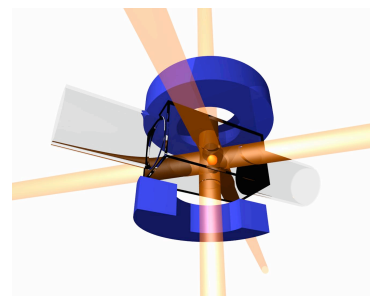
$$T \sim \frac{\hbar^2 n^{2/3}}{mk_{\text{B}}} \sim 100\text{nK to a few } \mu\text{K}.$$

<sup>9</sup>Here, by thermodynamic, we mean that the fraction scales in proportion to the density.

<sup>10</sup>The Bose-Einstein condensate was first predicted by Satyendra Nath Bose and Albert Einstein in 1924-25. Bose first sent a paper to Einstein on the quantum statistics of light quanta (now called photons). Einstein was impressed, translated the paper himself from English to German and submitted it for Bose to the Zeitschrift fr Physik which published it. Einstein then extended Bose’s ideas to material particles (or matter) in two other papers.

Note that,

$$\int_0^\infty dx \frac{x^2}{e^x - 1} = 2\zeta(3) \sim 2.404.$$



Schematic of a Magneto-Optical Trap (MOT). The invention of the MOT in 1987 at Bell Labs and optical molasses was the basis for the 1997 Nobel Prize in Physics.

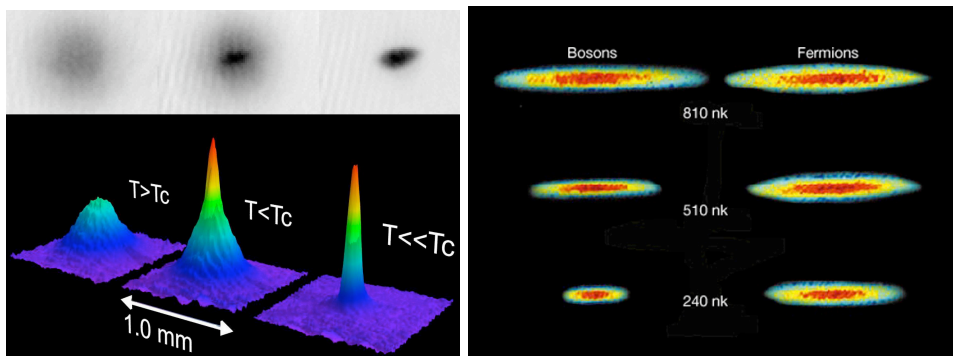


Figure 8.2: (Left) Observation of BEC by absorption imaging. The top row shows shadow pictures, which are rendered in a 3d plot below. The “sharp peak” is the BEC, characterized by its slow expansion observed after 6 ms time of flight. The total number of atoms at the phase transition is about  $7 \times 10^5$ , and the temperature at the transition point is  $2 \mu\text{K}$ . (Figure from Ketterle.) (right) Figure shows the shrinking of the atom cloud in a magnetic as the temperature is reduced by evaporative cooling. Comparison between bosonic  ${}^7\text{Li}$  (left) and fermionic  ${}^6\text{Li}$  (right) shows the distinctive signature of quantum statistics. The fermionic cloud cannot shrink below a certain size determined by the Pauli exclusion principle. This is the same phenomenon that prevents white dwarf and neutron stars from shrinking into black holes. At the highest temperature, the length of the clouds was about 0.5mm. (Figure from J. R. Anglin and W. Ketterle, *Bose-Einstein condensation of atomic gases*, *Nature* **416**, 211 (2002).)

At these temperatures the atoms move at speeds of  $\sim \sqrt{k_B T/m} \sim 1 \text{ cm s}^{-1}$ , which should be compared with around  $500 \text{ ms}^{-1}$  for molecules at room temperature, and  $\sim 10^6 \text{ ms}^{-1}$  for electrons in a metal at zero temperature. Achieving the regime  $n_T^3 \sim 1$ , through sufficient cooling, is the principle experimental advance that gave birth to this new field of physics.

It should be noted that such low densities of atoms are in fact a necessity. We are dealing with systems whose equilibrium state is a solid (that is, a lump of Sodium, Rubidium, etc.). The first stage in the formation of a solid would be the combination of pairs of atoms into diatomic molecules, but this process is hardly possible without the involvement of a third atom to carry away the excess energy. The rate per atom of such three-body processes is  $10^{29} - 10^{30} \text{ cm}^6 \text{ s}^{-1}$ , leading to a lifetime of several seconds to several minutes. These relatively long timescales suggest that working with equilibrium concepts may be a useful first approximation.

Since the alkali elements have odd atomic number  $Z$ , we readily see that alkali atoms with odd mass number are bosons, and those with even mass number are fermions. Thus bosonic and fermionic alkalis have half-integer and integer nuclear spin respectively. Alkali atoms have a single valence electron in an  $ns$  state, so have electronic spin  $J = S = 1/2$ . The experimental star players: are shown in the table (right). The hyperfine coupling between electronic and nuclear spin splits the ground state manifold into two multiplets with total spin  $F = I \pm 1/2$ . The Zeeman splitting of these multiplets by a magnetic field forms the basis of magnetic trapping.

So, based on our discussion above, what happens when a Bose or Fermi gas is confined by an harmonic trapping potential,  $V(\mathbf{r}) = \frac{1}{2}m\omega^2 r^2$ . At high temperatures, Bose and Fermi gases behave classically and form a thermal (Gaussian) distribution,  $P(r) \simeq e^{-m\omega^2 r^2/2k_B T}$ . As the system is cooled towards the point of quantum degeneracy, i.e. when the typical separation between particles,  $n^{-1/3}$ , becomes comparable to the thermal wavelength,  $\lambda_T$ , quantum statistics begin to impact. In the Fermi system, Pauli exclusion leads to the development of a Fermi surface and the cloud size becomes arrested. By contrast, the Bose system can form a BEC, with atoms condensing into the ground state of the harmonic potential. Both features are shown in Figure 8.2.

Bosons		Fermions	
${}^7\text{Li}$	$I=3/2$	${}^6\text{Li}$	$I=1$
${}^{23}\text{Na}$	$I=3/2$	${}^{23}\text{K}$	$I=4$
${}^{87}\text{Rb}$	$I=3/2$		