5.1 Two-Particle Systems

We encountered a two-particle system in dealing with the addition of angular momentum. Let's treat such systems in a more formal way.

The w.f. for a two-particle system must depend on the spatial coordinates of *both* particles as well as t: $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$, satisfying $i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$, where $H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$, and $\int d^3\mathbf{r}_1 d^3\mathbf{r}_2\, |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 = 1$.

Iff V is independent of time, then we can separate the time and spatial variables, obtaining $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2) \exp(-iEt/\hbar)$, where E is the total energy of the system.

Let us now make a very fundamental assumption: that each particle occupies a one-particle e.s. [Note that this is often a *poor* approximation for the *true* many-body w.f.] The joint e.f. can then be written as the product of two one-particle e.f.'s: $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$.

Suppose furthermore that the two particles are indistinguishable. Then, the above w.f. is not really adequate since you can't actually tell whether it's particle 1 in state a or particle 2. This indeterminacy is correctly reflected if we replace the above w.f. by $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)$. The 'plus-or-minus' sign reflects that there are two distinct ways to accomplish this. Thus we are naturally led to consider two kinds of identical particles, which we have come to call 'bosons' $(+)$ and 'fermions' $(-)$.

It so happens that all particles with *integer* spins are bosons (*e.g.*, photons, mesons) and all particles with *half-integer* spins are fermions (*e.g.*, electrons, protons). This connection between ‘spin’ and ‘statistics’ can be proven in relativistic quantum mechanics, but must be accepted as axiomatic in the nonrelativistic theory.

It follows from the form of the w.f. that two identical fermions cannot occupy the same state (*e.g.*, ψ_a) because then the ‘antisymmetric’ wavefunction would be identically zero. This is simply the Pauli exclusion principle.

Let’s define an ‘exchange’ operator, P, $\ni Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$. $P^2 = 1$, so the e.v. of $P = \pm 1$. Furthermore, two identical particles must be treated identically by the Hamiltonian $\Rightarrow$ $[P, H] = 0$. Thus we can find e.s. of H which are also e.s. of P; *i.e.*, either symmetric or antisymmetric under exchange: $\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_2, \mathbf{r}_1)$. Like its spin, this symmetry property is intrinsic to a particle, and *cannot* be changed.

The ramifications of this symmetry property can be illustrated with a simple one-dimensional example.

Suppose we ask for the expectation value of $(x_1 - x_2)^2$ in three distinct states: (1) distinquishable particles; indistinguishable particles which are (2) bosons and (3) fermions.

(1) distinguishable particles,
$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$:
$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$.

(2,3) indistinguishable particles,
$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2)$:
$\langle (x_1 - x_2)^2 \rangle_\pm = \langle (x_1 - x_2)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2$, where
$\langle x \rangle_{ab} \equiv \int dx\, x \psi_a^*(x)\psi_b(x)$.

We conclude that bosons are found closer to one another than are distinguishable particles, while fermions are found further apart. Other properties are similarly affected.

The above effect is *not* the result of an actual physical force, but it does *appear* as though bosons are attracted to one another and fermions are repelled by one another. It is therefore common, if misleading, to refer to this effect as arising from an ‘exchange force’.

In principle, every particle is linked to every other *indistinguishable* particle in the universe. Fortunately for us, the last term is *very* small without an appreciable overlap of ψ_a with ψ_b, and can be neglected in many cases *in practice*.

We presume that there is no coupling between the spin and position of particles, which leads to the separability of these coordinates and the property that the w.f. can be written as a product of a spin and a spatial part: $\psi(\mathbf{r})\chi(\mathbf{s})$.

It follows, then, that the requirement that fermions occupy antisymmetric w.f.'s refers to this product of the spatial and spin parts. Thus, a symmetric spin state (*e.g.*, a triplet) must be associated with an antisymmetric spatial w.f. (an antibonding combination), while an antisymmetric spin state (*e.g.*, a singlet) must be associated with a symmetric spatial w.f. (a bonding combination).

Figure 5.1 - Covalent bond: (a) symmetric combination produces attractive force; (b) antisymmetric combination produces repulsive force.

Atoms

For a neutral atom,

$$H = \sum_{j=1}^{Z} \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right) + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^{Z} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}.$$

For fermions, the spatial part of the w.f. must satisfy $H\psi = E\psi$ and the complete w.f. $\phi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_Z)$ must be antisymmetric with respect to the exchange operator.

For hydrogen, $Z = 1$, so there is no contribution from the electron–electron interaction term. ϕ is then simply a one-electron w.f.

For helium, $Z = 2$, leading to a single electron–electron interaction term. This is enough to turn the proper solution of the Schrödinger equation into a true many-body w.f.

Setting aside that complication for the moment, let's assume that the spatial portion of the w.f. can be approximated as the product of two one-electron w.f.'s: $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$, where the Bohr radius is half as large as for hydrogen and $E = 4(E_n + E_{n'})$, $E_n = -\frac{13.6}{n^2}$ eV.

Specifically, the ground state is $\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$ and $E_0 = -109$ eV.

Because ψ_0 is a symmetric function, the spin w.f. must be antisymmetric. Thus, the ground state of He is a *singlet* configuration, wherein the spins are aligned oppositely.

The actual ground state is indeed a singlet, but the energy is only -79 eV. Such poor agreement is expected since we neglected the positive (repulsive) contribution of electron–electron interaction.

The excited states of He consist of one electron in the hydrogenic ground state and the other in an excited state: $\psi_{nlm}\psi_{100}$. The spatial portion of this w.f. can be constructed either symmetrically or antisymmetrically $(\psi_a\psi_b \pm \psi_b\psi_a)$, leading to the possibility of either antisymmetric or symmetric spin portions, respectively, known as *parahelium* and *orthohelium*.

If you try to put both electrons in excited states, one immediately drops into the ground state, releasing enough energy to knock the other electron into the continuum and yielding a He ion (He$^+$). This process is known as an *Auger* transition.

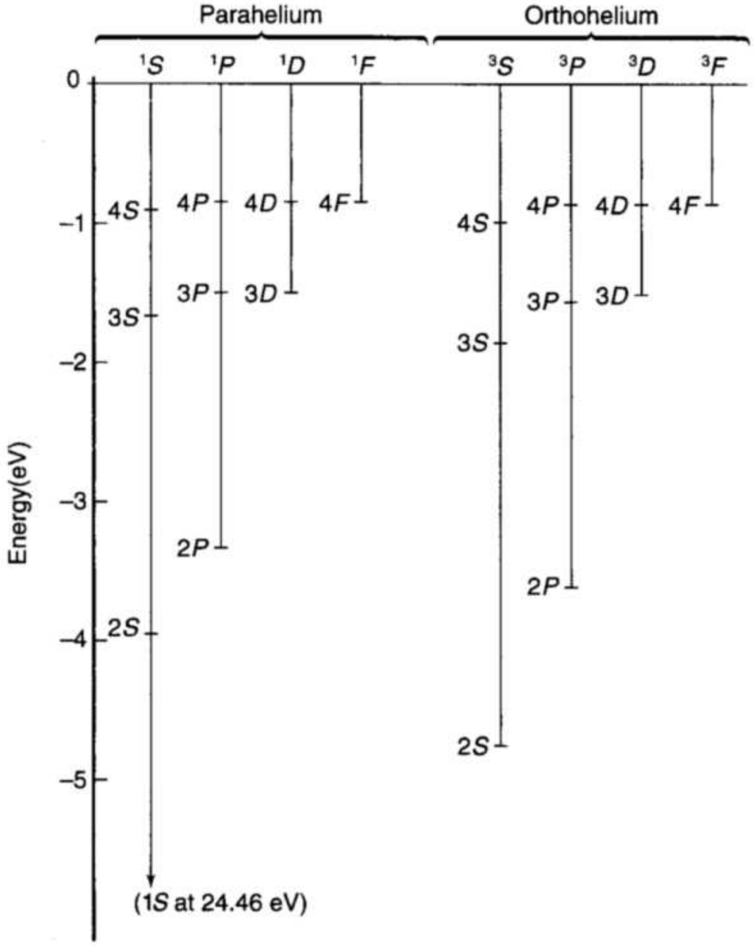

Figure 5.2 - Energy level diagram for He (*relative* to He$^+$, -54.4 eV). Note that parahelium (*antisymmetric* spin) energies are uniformly higher than orthohelium counterparts.

For heavier atoms we proceed in the same way. To a first approximation, the w.f. are treated by placing electrons in one-electron, hydrogen-like states (nlm) called orbitals. Since electrons are fermions, only two of them (having opposite spins, the singlet configuration) can occupy each orbital. There are n^2 hydrogenic w.f.'s for a given n, all with same e.v..

These would correspond to the rows in the periodic table, except that including the electron–electron repulsion raises the energy of large l states more than small l states. This effect arises because the 'centrifugal term' in the radial equation pushes the wavefunction out and is larger for large l. Furthermore, in the outer regions, the charge of the nucleus becomes increasing screened by the inner electrons. In practice, it raises the energy of, *e.g.*, the $nlm = 3\,2\,m$ above that of $4\,0\,m$ and modifies the positions thereafter.

Note that the states with $l = 0, 1, 2, 3, ...$ are usually referred to by the letters $s, p, d, f, ...$ Thus a $nl = 3\,2$ state is often referred to as a $3d$ state.

Study of the (empirically-derived) periodic table has led to additional rules for the energy ordering of states with varying total orbital angular momentum (L), and also varying values of total spin (S) and total orbital plus spin angular momentum (J). See text for details.

5.3 Solids

In the solid state, some of the loosely-bound electrons in each atom become detached, roam ‘freely’ amongst the atoms, and are known as conduction electrons. The remaining electrons on each atom form the ‘core’, and are changed only slightly by the overlapping potentials of the other atoms. Let us consider two simple models for the conduction electron e.s.

Sommerfeld's free electron gas

Assume that the conduction electrons are not subject to any potential variations at all, except that they are confined absolutely within a 'large' rectangular solid of dimensions l_x, l_y, l_z:

$$V(x,y,z) = \begin{cases} 0 & \text{if}(0 < x < l_x, 0 < y < l_y, 0 < z < l_z) \\ \infty & \text{otherwise} \end{cases}$$

As before, the Schrödinger equation can be solved using separation of variables, yielding $\psi(\mathbf{k}) = \sqrt{\frac{8}{\Omega}} \sin k_x x \sin k_y y \sin k_z z$, where $E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$, $k_i \equiv \frac{n_i \pi}{l_i}$, $n_i = 1, 2, 3, \ldots$, and $\Omega \equiv l_x l_y l_z$.

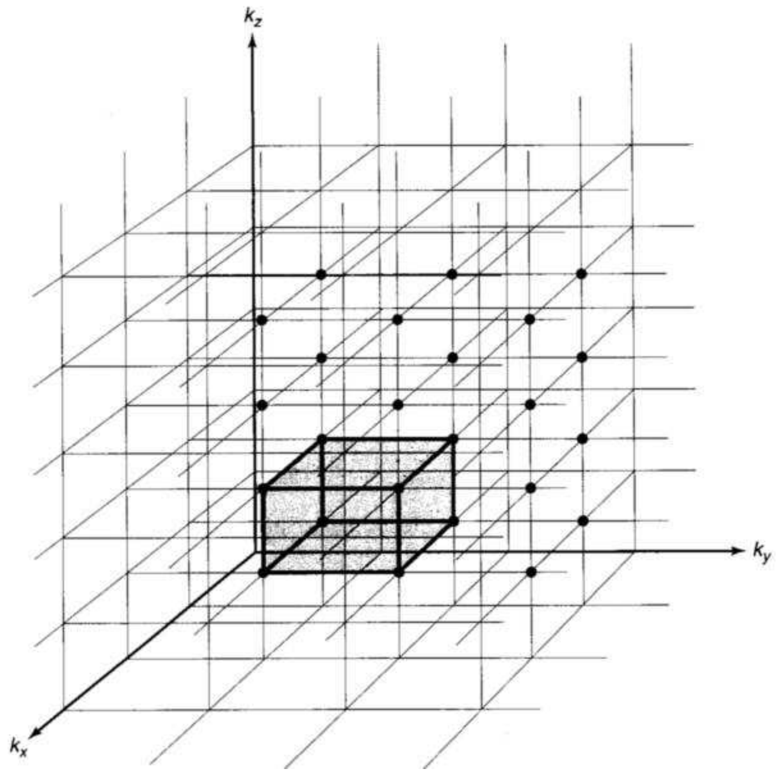

Figure 5.3 - Free electron gas. Each intersection represents one allowed energy. Shaded block is volume occupied by one *state*.

Suppose this solid contains N atoms [a number on the order of Avogadro's number, $\sim 10^{27}$ atoms/m^3], each one of which contributes one or more electrons to the 'Fermi sea'. If the solid is in its ground state and the electrons were bosons or distinguishable particles, they would all occupy the lowest energy state, 111.

But electrons are actually fermions, so only two electrons (with opposite spins) can occupy each of the states we have identified. In the ground state, they will occupy $N_e/2$ of the lowest energy states, filling a *sphere* in k-space of radius $k_F = (3\rho\pi^2)^{1/3}$, where k_F is the Fermi vector, $\rho = \frac{N_e}{\Omega}$, and N_e is the total number of 'free' electrons in the solid.

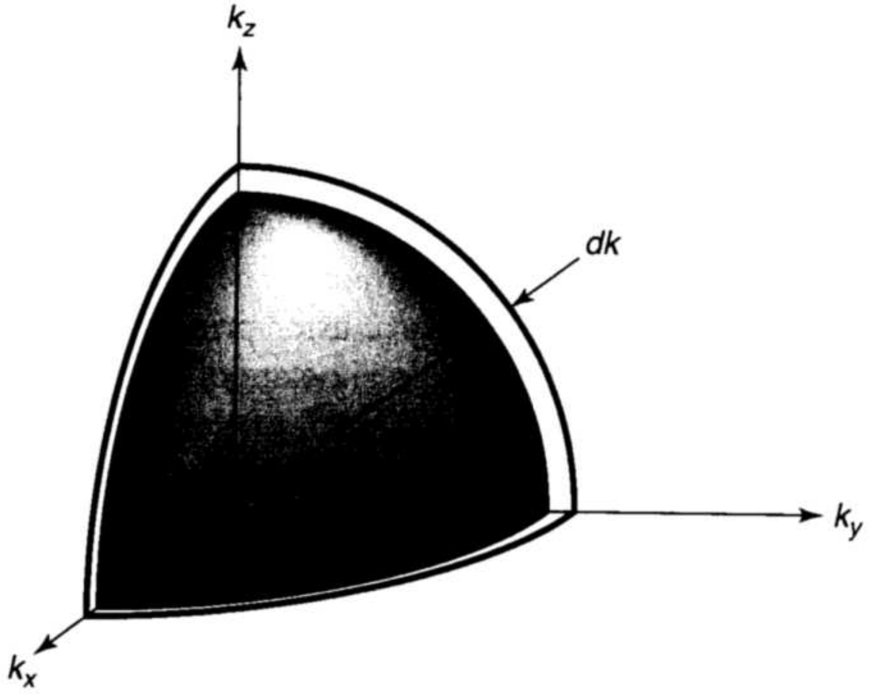

Figure 5.4 - One octant of a spherical shell in *k*-space.

The boundary surface (in k-space) between the occupied and unoccupied states is called the Fermi surface, while the energy of the highest occupied state is called the Fermi energy, $E_F = \frac{\hbar^2 k_F^2}{2m}$. Since we know the properties of the e.s, we can calculate the total energy of the conduction electrons: $E_{total} = \frac{\hbar^2 k_F^5 \Omega}{10\pi^2 m}$.

If we include the volume-dependence of the Fermi vector, $E_{total} \propto \Omega^{-2/3}$, and increases if the volume decreases. This effect, which arises completely from the quantum-mechanical requirement that the wavefunctions be antisymmetric under exchange, acts like a pressure: $P = \frac{2}{3}\frac{E_{total}}{\Omega}$.

Note also that we have included neither the electron–atom core nor the electron–electron interactions at this point.

Bloch model of a periodic solid

Consider a one-dimensional, periodic solid. Bloch's theorem says that $V(x + a) = V(x) \Rightarrow \psi(x + a) = e^{iKa}\psi(x)$.

If we use periodic boundary conditions on the entire macroscopic solid containing N potentials, $\psi(x) \Rightarrow \psi(x + Na) = e^{iNKa}\psi(x)$, so that $K = \frac{2\pi n}{Na}, (n = 0, \pm 1, \pm 2, \ldots)$.

Thus we have a prescription for obtaining the e.f. everywhere once we have solved for it within a single cell.

To see more, we must choose a specific potential. Consider what is arguably the simplest periodic potential: a one-dimensional evenly-spaced array of Dirac δ-functions, $V(x) = -\alpha \sum_j \delta(x - ja)$, called a *Dirac comb*.

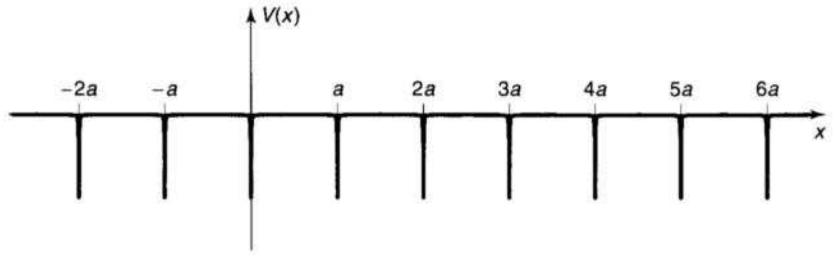

Figure 5.5 - The ‘Dirac comb’.

In the regions between the δ-functions, the e.s.’s have $E = \frac{\hbar^2 k^2}{2m}$ and functional forms like $\sin(kx)$. Specifically, for the cells to the left and right of the δ-function at the origin, the Bloch form requires that $\psi(x) = A\sin(kx) + B\cos(kx), (0 < x < a)$ and

$\psi(x) = e^{-iKa}[A\sin(kx)+B\cos(kx)], (-a < x < 0)$.

Since the δ-functions are non-zero only at a point, the resulting w.f.’s are continuous through them but the derivatives are discontinuous, satisfying a boundary condition obtained by integrating the differential equation once (see Chap. 2). Thus $A\sin(ka) = [e^{iKa} - \cos(ka)]B$ and $\cos(Ka) = \cos(ka) - \frac{m\alpha}{\hbar^2 k}\sin(ka)$.

The allowed E and k are determined by the last equation. Note that the obvious requirement that $|\cos(Ka)| \leq 1$ leads to the existence of values of k for which that equation *cannot* be satisfied. This can be seen by graphing the rhs of the equation against $z = ka$, letting $\frac{m\alpha a}{\hbar^2} = 10$.

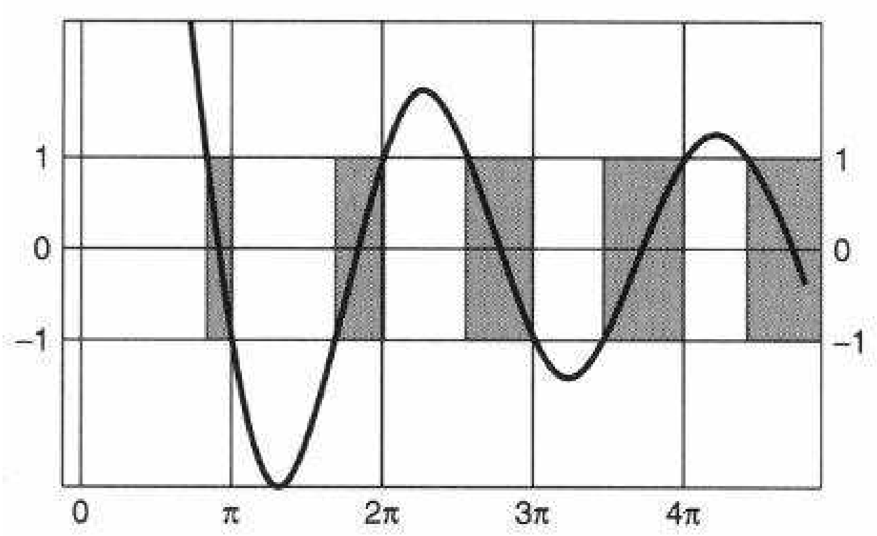

Figure 5.6 - A graph of the rhs of the equation for $\cos(Ka)$. Solutions exist only for $|\cos(Ka)| \leq 1$.

Thus there are regions of the energy spectrum for which there are no solutions, referred to as *gaps* in the density of states. These gaps are separated by nearly continuous bands of allowed states, each band containing N states. The division of the energy spectrum into bands of allowed states separated by gaps is a general characteristic of periodic potentials, and is referred to as the band structure.

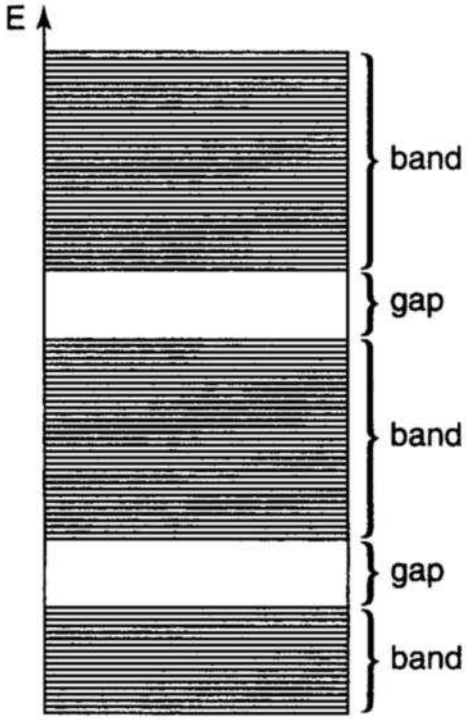

Figure 5.7 - The allowed positive energies for a periodic potential.

Once the band structure has been determined, in the ground state the electrons occupy the lowest energy $N_e/2$ levels. If, as a result, the topmost band containing electrons is only partially filled, a metal or conductor is the consequence. If, on the other hand, the topmost band is completely filled, so that conduction results only from those electrons excited into the next band, an insulator or semiconductor results, depending on the size of the gap.

5.4 Quantum Statistical Mechanics

So far, we have been dealing with the ground state of systems. Statistical mechanics deals with the occupation of states when a system is excited. The fundamental assumption of statistical mechanics is that, in *thermal equilibium*, every *distinct* state with the same total energy is occupied with equal probability. Temperature is simply a measure of the total energy of a system in thermal equilibium.

The only change from *classical* statistical mechanics occasioned by quantum mechanics has to do with how we count distinct states, which depends on whether the particles involved are distinguishable, identical fermions, or identical bosons.

Three non-interacting particles

Suppose we have three non-interacting particles, all of mass m, occupying a one-dimensional square well: $E_{total} = \frac{\pi^2\hbar^2}{2ma^2}(n_A^2 + n_B^2 + n_C^2)$. Suppose further than the total energy of this system corresponds to $n_A^2 + n_B^2 + n_C^2 = 243$.

There are 13 distinct combinations of 3 positive integers such that the sum of their squares is 243: $(9,9,9), (3,3,15), (3,15,3), (15,3,3)$, $(11,11,1), (11,1,11), (1,11,11)$, $(5,7,13), (5,13,7), (13,5,7)$, $(7,5,13), (7,13,5), (13,7,5)$.

Distinguishable particles: each of the above 13 represents a distinct quantum state, and each would occur with equal probability. For example, particle A has a 2/13 chance of being in 3. $\therefore P_1 = P_9 = P_{15} = 1/13$ and $P_3 = P_5 = P_7 = P_{11} = P_{13} = 2/13$, the remainder being zero. Note that $\sum P_i = 1$.

Identical fermions: leaving spin aside for simplicity, the antisymmetrization requirement eliminates all states in which two or more particles occupy the same level (*i.e.*, value of n). This eliminates the first 7 states, leaving 6 equally occupied states, or $P_5 = P_7 = P_{13} = 1/3$, the remainder being zero.

Identical bosons: the symmetrization requirement allows one state with each configuration, of which there are 4:
$P_9 = 1/4; P_3 = P_{11} = (1/4) \times (2/3)$;
$P_1 = P_{15} = (1/4) \times (1/3)$;
$P_5 = P_7 = P_{13} = (1/4) \times (1/3)$; the remainder being zero.

So, the results vary dramatically depending on the fundamental nature of the particles.

General case

Consider an arbitrary potential, for which the one-particle energies are $E_1, E_2, E_3, \ldots$ with degeneracies $d_1, d_2, d_3, \ldots$. If we put N particles into this potential, the number of distinct states corresponding the configuration $(N_1, N_2, N_3, \ldots)$ is Q, where we expect Q to be a strong function of whether the particles are distinguishable, identical fermions, or identical bosons. After a detailed consideration of the numbers of particles and states, the following formulae for Q result.

Distinguishable particles:

$$Q(N_1, N_2, N_3, \ldots) = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}.$$

Identical fermions:

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}.$$

Identical bosons:

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}.$$

⁂

In thermal equilibrium, the most probable configuration is that one which can be attained in the largest number of different ways. We want to find this subject to two constraints:

$$\sum_{n=1}^{\infty} N_n = N \quad \text{and} \quad \sum_{n=1}^{\infty} N_n E_n = E.$$

This is best handled using Lagrange multipliers. It is also useful to maximize $\ln(Q)$ rather than Q, which turns the products of factorials into sums. Let

$$G \equiv \ln(Q) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right],$$

where α and β are the Lagrange multipliers. We now seek the values of N_n which satisfy $\frac{\partial G}{\partial N_n} = 0$, $\frac{\partial G}{\partial \alpha} = 0$, and $\frac{\partial G}{\partial \beta} = 0$.

The most probable occupation numbers are:

Distinguishable particles: $N_n = d_n e^{-(\alpha+\beta E_n)}$.

Identical fermions: $N_n = \frac{d_n}{e^{(\alpha+\beta E_n)}+1}$.

Identical bosons: $N_n = \frac{d_n}{e^{(\alpha+\beta E_n)}-1}$.

Physical significance of α and β

Insight into the physical meaning of α and β can be gained by substituting one of the above equations for N_n into the sums which yield N and E, but that requires assuming a specific model for V. Let's use a simple V, a three-dimensional infinite square well:

For distinguishable particles,

$$e^{-\alpha} = \frac{N}{V}\left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2} \text{ and } E = \frac{3N}{2\beta}.$$

The second equation leads us to *define* T by $\beta \equiv \frac{1}{k_B T}$. α is customarily expressed in terms of a *chemical potential*: $\mu(T) \equiv -\alpha k_B T$.

With these definitions, which turn out to be sensible and useful in the general case, we can now write expressions for the most probable number of particles in a *particular* one-particle state with energy ε as:

Distinguishable particles (Maxwell-Boltzmann):
$n(\varepsilon) = e^{-(\varepsilon-\mu)/k_B T}$.

Identical fermions (Fermi-Dirac):
$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T}+1}$.

Identical bosons (Bose-Einstein):
$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T}-1}$.

These are the familiar occupation probabilities.

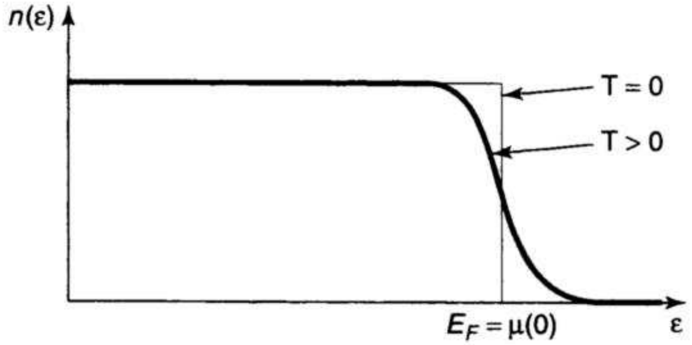

Figure 5.8 - The Fermi-Dirac distribution for $T = 0$ and for T somewhat above zero.

Finally, it is possible to work out somewhat more fully the relationships which lead to T and μ:

Distinguishable particles: $E = \frac{3}{2} N k_B T$ and

$$\mu(T) = k_B T \left[\ln \left(\frac{N}{V} \right) + \frac{3}{2} \ln \left(\frac{2\pi\hbar^2}{m k_B T} \right) \right].$$

For the other cases, the integrals cannot be evaluated in terms of elementary functions.

Identical particles:

$$N = \frac{V}{2\pi^2} \int_0^\infty dk \frac{k^2}{e^{[(\hbar^2 k^2/2m) - \mu]/k_B T} \pm 1}$$

$$E = \frac{V}{2\pi^2} \frac{\hbar^2}{2m} \int_0^\infty dk \frac{k^4}{e^{[(\hbar^2 k^2/2m) - \mu]/k_B T} \pm 1},$$

where, as usual, the upper sign is for fermions and the lower for bosons.

Blackbody spectrum

Photons are identical bosons with spin 1, but they are a very special case because they are *massless*. Thus they are intrinsically relativistic. We must therefore accept as assertions four of their properties which do not really belong in nonrelativistic quantum mechanics:

(1) The energy of a photon is related to its frequency by the Planck formula: $E = \hbar\omega$.

(2) The wavenumber k is related to the frequency by $k = 2\pi/\lambda = \omega/c$, where c is the speed of light.

(3) Only two spin states can occur; *i.e.*, m can be ± 1, but never 0.

(4) The number of photons is not a conserved quantity; the number (per unit volume) increase as T increases.

In view of item (4), we cannot constrain the number of photons. Setting $\alpha = 0$, the most probable number of photons is

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_B T} - 1}.$$

For free photons in a box of volume V,

$$d_k = \frac{V}{\pi^2 c^3}\omega^2 d\omega,$$

where we have multiplied by 2 for spin.

This leads to the energy density

$$\rho(\omega) = \frac{N_\omega \hbar\omega}{V} = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)},$$

which is Planck's blackbody spectrum, one of the early successes of quantum physics.

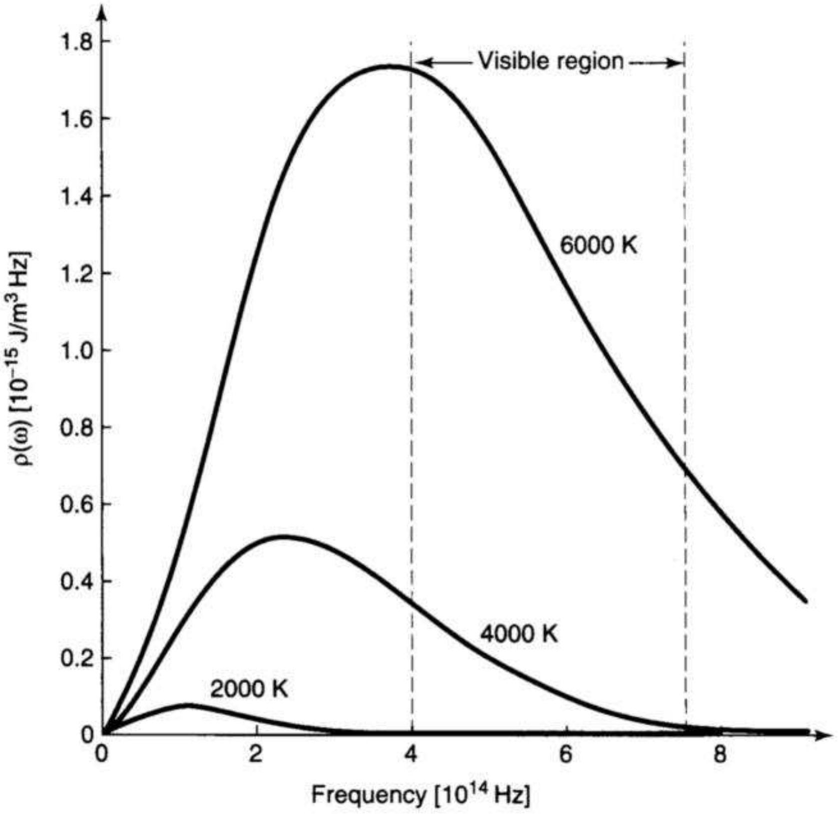

Figure 5.9 - Planck's blackbody spectrum.