few times 10^3 cm^{-1}, so that electron positions can be specified to within 10μ or so without appreciably disturbing thermal equilibrium.

Any two of these wave packets, differing in the number n, which specifies location, or in m, which specifies momentum, or both, are orthogonal states, and therefore count, for the Pauli principle, as distinct states of motion.

In problems of the present kind, which involve counting states, it pays to avoid surprises on an altogether lower level, by keeping in mind the distinction between the "box" boundary condition we have used, and the cyclic boundary condition, which is often more convenient.

With the latter choice we require wave functions which repeat after a distance L. If these are written in the form $\exp(ikx)$, k must be a multiple of $2\pi/L$. The spacing of permissible k values is therefore twice what we had in the box, but we must remember that there was, for the box, no point in letting k become negative, whereas now $\exp(ikx)$ and $\exp(-ikx)$ are distinct functions. For counting up the states in a given energy range, i.e., within a given range of k^2, the cyclic boundary condition gives us half the density of states, but spread over two equal intervals in k. Overall, both schemes therefore give the same answer if we apply each consistently.

3.2. IONIZATION

If atoms are in statistical equilibrium at a temperature T, in circumstances in which the interaction between atoms is negligible, the probability of an atom being in the state n is given by Boltzmann's expression

$$\frac{1}{Z} e^{-\beta E_n},\tag{3.2.1}$$

where, as usual,

$$\beta = 1/KT,\tag{3.2.2}$$

K being Boltzmann's constant, and

$$Z = \sum_n e^{-\beta E_n}, \qquad (3.2.3)$$

the sum to extend over all states, and to include an integration over the continuous spectrum.

At low temperature, when one is interested mainly in states of low excitation, the relative probabilities of occupation can easily be read off from (3.2.1). However, even at low temperature, we cannot get absolute values, because the sum for Z in (3.2.3) diverges. This is true even for the contribution from the discrete spectrum. For example, in hydrogen there are, counting spin, $2n^2$ states of energy

$$E_n = -\frac{R}{n^2}, \quad n = 1, 2, 3, \ldots, \qquad (3.2.4)$$

where R is Rydberg's constant. These tend to 0 for large n, so the discrete sum for Z diverges as $\sum 2n^2$. The contribution of the continuous spectrum makes the divergence even worse.

We have to conclude, with some surprise, that the chance of the atom remaining in the ground state or in any other finite state is zero. To make this a little more quantitative, consider an atom in a finite volume, say a sphere of radius a. Then states extending over a radius much less than a will have the same energy as in free space, and states extending much beyond a will not exist. Since the mean radius is $a_0 n^2$, with a_0 the Bohr radius, we can find the right order of magnitude by cutting off the sum at $n = (a/a_0)^{1/2}$, which, for large a, gives $\frac{2}{3}(a/a_0)^{3/2}$. On the other hand, it is easy to see that the continuous spectrum contributes, in the same limit, an amount proportional to the volume, i.e., to a^3. So in a really large volume the dominant state for the electron is to be in a state of positive energy; the atom is ionized.

If we are really dealing with a single atom in an infinite volume, this is physically the correct answer, because the equilibrium for

ionization depends on the available volume. This is evident from the consideration of the rate of ionization and recombination, which must balance in equilibrium. Whatever the mechanism, the rate of ionization is independent of the volume, whereas the rate of recombination depends on the chance of the electron meeting the nucleus again, which is inversely proportional to the volume.

In practical problems we are more often concerned with a large number of atoms in a large volume at finite, if perhaps low, density. In that case, we can use the eigenstates of the free atom only if their extension is less than the mean spacing between atoms, and we should, for each atom, not count states of a greater extension, since these overlap other atoms, and are then, in fact, approximated by the states of the other atoms, which will also be included. Similarly we must not attribute a continuous spectrum to each atom, since this would also involve double-counting. At low density, the continuous spectrum can be replaced by electrons moving in free space. Finally, we must allow for the mutual repulsion of the electrons, which means that the binding energy of an electron in the atom is substantially reduced if there is another electron in it already.

The full discussion, given, for example, very clearly in Landau and Lifshitz, *Statistical Physics*, §103, shows that, at temperatures at which the atom is not almost completely ionized, the excitation probability is negligible, so that one is concerned only with atoms in the ground state, ions (i.e., for hydrogen bare protons), and free electrons. The equilibrium can then be determined by the usual methods for finding the equilibrium in a reaction. The result given by Landau and Lifshitz takes, for hydrogen, the form that the degree of ionization, i.e., the ratio between the number of ions and that of all nuclei, is

$$\alpha = \left\{ 1 + \frac{P}{KT} \left(\frac{2\pi\hbar^2}{mKT} \right) e^{-\beta R} \right\}^{-1/2}, \qquad (3.2.5)$$

where P is the pressure, and m the electron mass.

We verify again that for infinite volume with a finite number of atoms, $P = 0$, the degree of ionization becomes complete at any temperature.

Historical note: The theory of thermal ionization was, I believe, first given by Saha, and the result used to be known as Saha's equation. It is still referred to as such by astrophysicists, but tends to be ignored in physics texts, with a few exceptions (such as the passage in Landau and Lifshitz referred to above). Physicists encountering this problem may therefore be tempted to fall into the trap which constituted our surprise here.

3.3. PERTURBATION THEORY FOR STATISTICAL EQUILIBRIUM

It is well known that all equilibrium properties of a system can be derived from the partition function Z, already defined in (3.2.3):

$$Z = \sum_n e^{-\beta E_n}, \quad \beta = \frac{1}{KT}. \tag{3.3.1}$$

In many cases, the energy eigenvalues E_n are not known exactly, and the Hamiltonian is of the form

$$H = H_0 + W \tag{3.3.2}$$

with only the eigenstates of H_0 known exactly. If W is small enough, we can find the eigenstates of H approximately by using a perturbation expansion, of which the first two terms are given by

$$E_n = E_n{}^0 + W_{nn} + \sum_{\substack{m \\ m \neq n}} \frac{|W_{nm}|^2}{E_n{}^0 - E_m{}^0}, \tag{3.3.3}$$

provided the unperturbed eigenvalues are all distinct. It is also known that, for the series to converge rapidly it is usually necessary that

$$|W| \ll \Delta E. \tag{3.3.4}$$