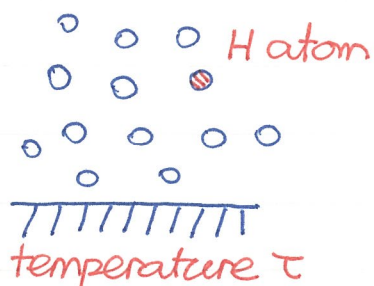


## HH0054 Multiplicity Function

Statistical physics is quantum in nature. To describe a system in thermal equilibrium, we need to know stationary quantum states of the system, often just called states !!

Ex: A hydrogen atom in thermal equilibrium stationary states  $|n\rangle$   $n=1S\uparrow, 1S\downarrow, 2S\uparrow, 2S\downarrow, \dots$



$$\langle O \rangle \equiv \sum_n P_n \langle n | O | n \rangle$$

need to learn quantum physics ☹

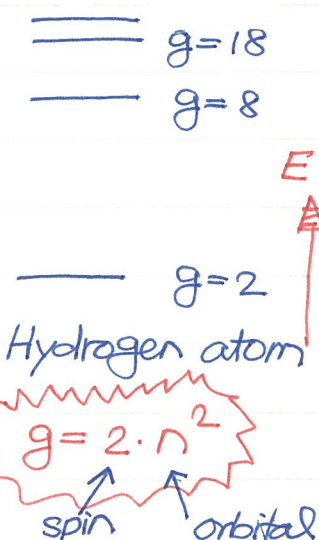
Boltzmann factor  $\propto e^{-E_n/\tau}$

Note that the expectation value of any observable in stationary quantum states doesn't vary with time  $\rightarrow$  equilibrium.

⬠ Multiplicity of an energy level. Plot all states out in energy  $\rightarrow$  energy levels.

Take H atom (just  $1 e^-$ ) as an examples.

There are more than one states associated with a particular energy  $E$ . The multiplicity is defined as the number of states at a particular energy level.



What about Lithium atom with 3 electrons? First of all, a quantum state is for all particles. BUT! Quantum states of a one-particle system are called orbitals. It is often convenient to label a many-particle state by orbitals.

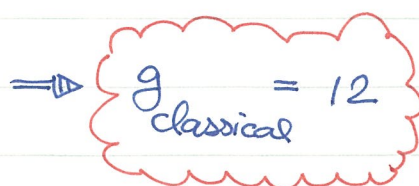


$(1S\uparrow, 1S\downarrow, 2S\uparrow), (1S\uparrow, 2S\uparrow, 1S\downarrow)$

$(1S\downarrow, 1S\uparrow, 2S\uparrow), (1S\downarrow, 2S\uparrow, 1S\uparrow)$

$(2S\uparrow, 1S\uparrow, 1S\downarrow), (2S\uparrow, 1S\downarrow, 1S\uparrow)$

plus additional 6 from  $(1S\uparrow, 1S\downarrow, 2S\downarrow)$



WRONG ☹

Electrons are identical particles. The correct counting is

$$|1s\uparrow, 1s\downarrow, 2s\uparrow\rangle, |1s\uparrow, 1s\downarrow, 2s\downarrow\rangle \quad \text{multiplicity } g=2$$

For excited lithium, one electron is kicked up to 2p orbital:

$$|1s^2, 2p_x\uparrow\rangle, |1s^2, 2p_y\uparrow\rangle, |1s^2, 2p_z\uparrow\rangle \\ |1s^2, 2p_x\downarrow\rangle, |1s^2, 2p_y\downarrow\rangle, |1s^2, 2p_z\downarrow\rangle \quad \underline{g=6} \text{ as in Kittel.}$$

Now, Boron with 5 electrons  $\dots$

ground state  $^2P$  ( $1s^2 2s^2 2p$ )  $\rightarrow l=1, s=\frac{1}{2}$

$$2p_x\uparrow, 2p_y\uparrow, 2p_z\uparrow, 2p_x\downarrow, 2p_y\downarrow, 2p_z\downarrow \Rightarrow \underline{g=6} \quad \leftarrow \text{Boron in ground state.}$$

1<sup>st</sup> excited state  $^4P$  ( $1s^2 2s 2p^2$ ), indicating  $l=1, s=\frac{3}{2}$

$$g = (2l+1)(2s+1) = 3 \cdot 4 = \underline{12}$$

2<sup>nd</sup> excited states  $^2S$  ( $1s^2 2s^2 3s$ )  $l=0, s=\frac{1}{2}$

$$g = (2l+1)(2s+1) = 1 \cdot 2 = \underline{2}$$

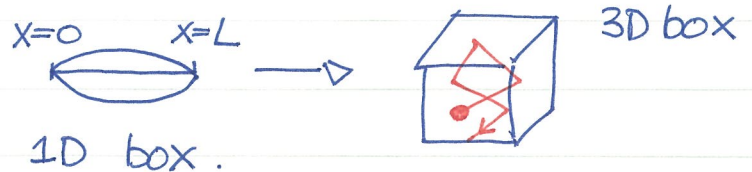
You get the idea that counting multiplicity  $g$  is not easy....  
In fact, read the recent paper [Physical Review A 83, 022505 (2011)] and you will find the excited states are not the same when compared with Figure 1.1 in Kittel.

## 2 Particle in a box

The wave number  $\vec{k}$  (and thus momentum  $\vec{p} = \hbar\vec{k}$ )

is quantized.

$$\rightarrow \begin{aligned} k_x L &= n_x \pi \\ k_x &= \frac{n_x \pi}{L} \end{aligned}$$



Similarly,

$$k_y = \frac{n_y \pi}{L}, \quad k_z = \frac{n_z \pi}{L}$$

The energy is quantized,

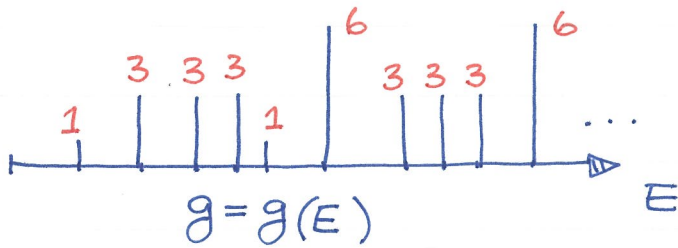
$$\mathcal{E} = \frac{1}{2m} (P_x^2 + P_y^2 + P_z^2) = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Now, work out the

multiplicity function  $g$ . ①  $(n_x, n_y, n_z) = (1, 1, 1) \rightarrow g = 1$

②  $(n_x, n_y, n_z) = (2, 1, 1), (1, 2, 1), (1, 1, 2) \rightarrow g = 3$  ③  $(n_x, n_y, n_z) = (2, 2, 1), (2, 1, 2),$

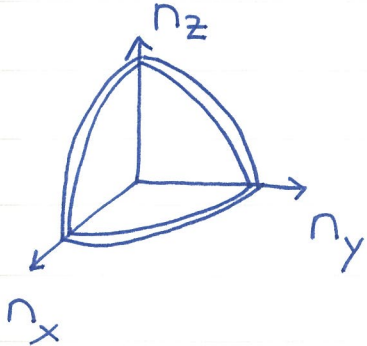
$(1, 2, 2) \rightarrow g = 3$  ④ and so on ...



The multiplicity function  $g(E)$  looks quite random. Besides, the spikes get closer and closer as  $L \rightarrow \infty$  !!

③ Continuous limit: In large  $L$  limit, a "continuous" description for multiplicity is in order.

$$\vec{n} = (n_x, n_y, n_z) \rightarrow n \equiv |\vec{n}| = \sqrt{n_x^2 + n_y^2 + n_z^2}, \quad \mathcal{E} = \frac{\pi^2 \hbar^2}{2mL^2} n^2$$



multiplicity in  $(E, E + \Delta E)$   
 $\equiv \sum_{E'} g(E')$ , where  $E' \in (E, E + \Delta E)$   
 $=$  enclosed grid points in the  $n$ -space

As long as  $\Delta E$  is small, it's natural to expect the sum proportional to  $\Delta E$ :

$$\sum_{E'} g(E') = D(E) \cdot \Delta E$$

Let's compute  $D(E)$  for one particle in 3D box.

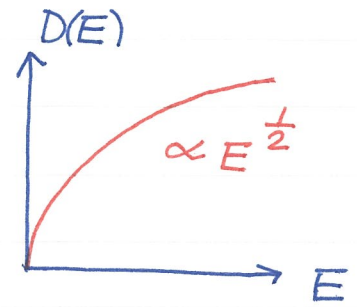
$\rightarrow$  density of states.

$$D(E) = \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \sum_{E'} g(E') = \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \cdot \frac{1}{8} (4\pi n^2) \cdot \Delta n$$

$$= \frac{\pi}{2} n^2 \frac{dn}{dE} \quad \text{Note that } n = \frac{\sqrt{2m} L}{\pi \hbar} \sqrt{E}$$

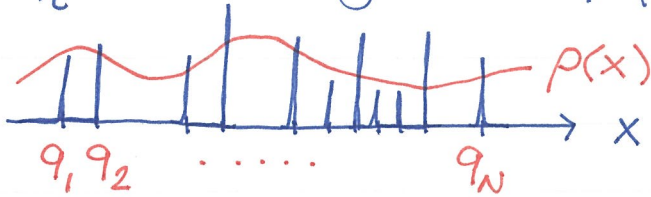
The density of states is

$$D(E) = \frac{\pi}{2} n^2 \frac{dn}{dE} = \frac{\pi}{4} \left( \frac{\sqrt{2mL}}{\pi\hbar} \right)^3 \sqrt{E}$$



Can you work out  $D(E)$  in 1D or 2D?

Compare  $g(E)$  and  $D(E)$  — very similar to discrete charges  $q_i$  and charge density  $\rho$ . One can introduce the charge



density

$$\rho(x) = \sum_{i=1}^N q_i \delta(x-x_i)$$

If the mutual distance between these discrete charges is small,  $\rho(x)$  can be viewed as a smooth function after coarse-graining. The total charge  $Q$  between  $(x_1, x_2)$  can be expressed as

$$Q = \sum_{i'} q_{i'} = \int_{x_1}^{x_2} dx \rho(x) \quad \text{where } i' \in (x_1, x_2)$$

Of course, if we choose  $x_2 = x_1 + \Delta x$ , the above relation

takes the form,  $\sum_{i'} q_{i'} = \rho(x_1) \Delta x$ ,  $i' \in (x_1, x_1 + \Delta x)$

It is very much

the same as the relation,  $\sum_{E'} g(E') = D(E) \Delta E$  ☺



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