Example: Spacing of lowest and second lowest orbitals of free atoms. The energy of an orbital of an atom free to move in a cube of volume $V = L^3$ is

$$\varepsilon = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (n_x{}^2 + n_y{}^2 + n_z{}^2) , \tag{57}$$

where n_x, n_y, n_z are positive integers. The energy $\varepsilon(111)$ of the lowest orbital is

$$\varepsilon(111) = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (1 + 1 + 1) , \tag{58}$$

and the energy $\varepsilon(211)$ of one of the set of next lowest orbitals is

$$\varepsilon(211) = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (4 + 1 + 1). \tag{59}$$

The lowest excitation energy of the atom is

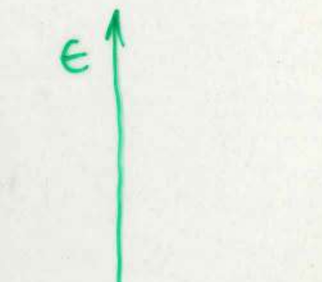
$$\Delta\varepsilon = \varepsilon(211) - \varepsilon(111) = 3 \times \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2. \tag{60}$$

If $M(^4\mathrm{He}) = 6.6 \times 10^{-24}\,\mathrm{g}$ and $L = 1\,\mathrm{cm}$,

$$\Delta\varepsilon = (3)(8.4 \times 10^{-32})(9.86) = \boxed{2.48 \times 10^{-30}\,\mathrm{erg}.} \tag{61}$$

In temperature units, $\Delta\varepsilon/k_B = 1.80 \times 10^{-14}\,\mathrm{K}$.

This splitting is extremely small, and it is difficult to conceive that it can play an important part in a physical problem even at the lowest reasonably accessible temperatures such as 1 mK, which is 10^{-3} K. However, at the 1 mK temperature (55) gives $\mu \simeq -1.4 \times 10^{-41}$ erg for $N = 10^{22}$ atoms, referred to the orbital (58) as the zero of energy. Thus μ is much closer to the ground orbital than is the next lowest orbital (59), and $\exp\{[\varepsilon(111) - \mu]/\tau\}$ is much closer to 1 than is $\exp\{[\varepsilon(211) - \mu]/\tau\}$, so that $\varepsilon(111)$ dominates the distribution function.



The Boltzmann factor $\exp(-\Delta\varepsilon/\tau)$ at 1 mK is

$$\exp(-1.8 \times 10^{-11}) \cong 1 - 1.8 \times 10^{-11} , \tag{62}$$

which is essentially unity. By (4) we would expect that even if $n \approx n_Q$ the occupancy of the first excited orbital would only be of the order of 1. However, the Bose-Einstein distribution gives an entirely different value for the occupancy of the first excited orbital:

$$f(\Delta\varepsilon,\tau) = \frac{1}{\exp[(\Delta\varepsilon - \mu)/\tau] - 1} \cong \frac{1}{\exp(\Delta\varepsilon/\tau) - 1} , \tag{63}$$