## Modern Physics

## Boltzmann

Problem 1.- Find the probability of finding the hydrogen atom in the low-lying hyperfine excited state at liquid helium temperature ( $\mathrm{T}=4.2 \mathrm{~K}$ ).
Approximate the atom as a two-level system where the energy of the excited state is $9.46 \times 10^{-25} \mathrm{~J}$ higher than the ground state and assume the degeneracies are 1 for the ground state and 3 for the first excited state.

Solution: According to Boltzmann the probability is:
$P_{2}=\frac{g_{2} e^{-E_{2} / k_{B} T}}{\sum g_{j} e^{-E_{j} / k_{B} T}}=\frac{g_{2} e^{-E_{2} / k_{B} T}}{g_{1} e^{-E_{1} / k_{B} T}+g_{2} e^{-E_{2} / k_{B} T}}=\frac{3 e^{-E_{2} / k_{B} T}}{1 e^{-E_{1} / k_{B} T}+3 e^{-E_{2} / k_{B} T}}=\frac{3 e^{-\left(E_{2}-E_{1}\right) / k_{B} T}}{1+3 e^{-\left(E_{2}-E_{B}\right) / k_{B} T}}$

Notice that: $\left(E_{2}-E_{1}\right) / k_{B} T=\frac{9.46 \times 10^{-25} J}{\left(1.38 \times 10^{-23} J / K\right)(4.2 K)}=0.016$
Which means that $e^{-\left(E_{2}-E_{1}\right) / k_{B} T}=0.984$, so the probability is:
$P_{1}=\frac{3(0.984)}{1+3(0.984)}=\mathbf{0 . 7 4 7}$

Notice that even at this low temperature, the excited state is very close to a simple $3 / 4$ probability, which would happen at high temperature.

Problem 1a.- Find the probability of finding the aluminum atom in the first excited state at room temperature ( $\mathrm{T}=300 \mathrm{~K}$ ). Approximate the atom as a two-level system where the energy of the first excited state is 0.0129 eV higher than the ground state and assume the degeneracies are 2 for the ground state and 4 for the first excited state.

Solution: According to Boltzmann the probability is:

$$
P_{2}=\frac{g_{2} e^{-E_{2} / k_{B} T}}{\sum g_{j} e^{-E_{j} / k_{B} T}}=\frac{g_{2} e^{-E_{2} / k_{B} T}}{g_{1} e^{-E_{1} / k_{B} T}+g_{2} e^{-E_{2} / k_{B} T}}=\frac{4 e^{-E_{2} / k_{B} T}}{2 e^{-E_{1} / k_{B} T}+4 e^{-E_{2} / k_{B} T}}=\frac{2 e^{-\left(E_{2}-E_{1}\right) / k_{B} T}}{1+2 e^{-\left(E_{2}-E_{1}\right) / k_{B} T}}
$$

Notice that: $\left(E_{2}-E_{1}\right) / k_{B} T=\frac{0.0129\left(1.6 \times 10^{-19} J\right)}{\left(1.38 \times 10^{-23} J / K\right)(300 K)}=0.499$
Which means that $e^{-\left(E_{2}-E_{1}\right) / k_{B} T}=0.607$, so the probability is:

$$
P_{1}=\frac{2 \times 0.607}{1+2 \times 0.607}=\mathbf{0 . 5 4 8}
$$

