8 — Excitation & Ionization [$Revision$: 1.3]

- Excitation
  - At absolute zero, all atoms of a given element are stationary, and electrons in each atom are in ground energy level. As temperature raised above zero, atoms undergo **thermal motions** ($mv^2/2 \approx 3kT/2$)
  - **Collisions** between moving atoms impart energy to electrons, **exctiting** them to higher energy level
  - Convention: label energy levels using index j:
    * $j = 1, 2, 3, \ldots$
    * $j = 1$ is ground level
    * E_j is energy of j'th level (j ordered so that $E_{j+1} > E_j$)
    * N_j is **level population** — number of atoms in level j
  - Each energy level can be composed of a number of **degenerate** (equal-energy) quantum states; this number is **statistical weight** g_j of level
  - Boltzmann statistics: at temperature T, probability an atom in energy level j:

    $$P_j \propto g_j \; e^{-E_j/kT}$$

  - For any pair of levels j and j', ratio of probabilities:

    $$\frac{P_{j'}}{P_j} = \frac{g_{j'}}{g_j} e^{-(E_{j'}-E_j)/kT}$$

  - Equivalent to ratio of level populations:

    $$\frac{N_{j'}}{N_j} = \frac{P_{j'}}{P_j} = \frac{g_{j'}}{g_j} e^{-(E_{j'}-E_j)/kT}$$

  - Because $\sum_{j=1} P_j = 1$,

    $$P_j = \frac{g_j e^{-(E_j-E_1)/kT}}{Z}$$

    where Z is **partition function**:

    $$Z = \sum_{j=1} g_j e^{-(E_j-E_1)/kT}$$

- Ionization
  - If enough energy given by collision, electron can be removed from atom — **ionization**
  - Convention: label ionization stages using index i:
    * $i = 1, 2, 3, \ldots, Z-1$ (where Z is atomic number)
    * $j = 1$ is neutral (unionized) stage
    * $E_{i,j}$ is energy of j'th level in i'th ionization stage
    * $g_{i,j}$ is corresponding statistical weight
    * χ_i is **ionization potential** of i'th stage — amount of energy to remove a further electron, and produce $i+1$'th stage
    * $N_{i,j}$ is number of atoms in stage i and level j
    * $N_i = \sum_j N_{i,j}$ is total number of atoms/ions in stage i

- Consider ionization but ignore excitation: all atoms/ions in ground level ($j = 1$)
- Ionization process: removing single electron from atom/ion in stage i, to produce ion in stage $i+1$ plus free electron. Can apply Boltzmann statistics — trick is to calculate statistical weights correctly
- For process producing free electron with momentum in interval $(p_\mathrm{e}, p_\mathrm{e}+\mathrm{d}p_\mathrm{e})$, ratio between numbers:
$$\frac{\mathrm{d}N_{i+1}}{N_i} = \frac{g_{i+1,1}\mathrm{d}g_\mathrm{e}}{g_{i,1}} e^{-(\chi_i + p_\mathrm{e}^2/2m_\mathrm{e})/kT}$$
(Note: energy term is sum of ionization potential χ_i and electron kinetic energy $p_\mathrm{e}^2/2m_\mathrm{e} = m_\mathrm{e}v_\mathrm{e}^2/2$). Electron statistical weight $\mathrm{d}g_\mathrm{e}$ is number of quantum states available to electron with momentum in interval $(p_\mathrm{e}, p_\mathrm{e} + \mathrm{d}p_\mathrm{e})$
- To calculate $\mathrm{d}g_\mathrm{e}$, use same approach as with blackbody radiation (see Notes 3):
    * Wave-particle duality: treat electrons as waves, number of states $\leftrightarrow$ number of permitted waves
    * In box with dimensions $\mathrm{d}V$, number of standing waves in wavenumber interval $(k, k+\mathrm{d}k)$:
    $$\mathrm{d}g_\mathrm{e} = \frac{k^2\mathrm{d}k}{\pi^2}\,\mathrm{d}V$$
    (Note: same expression as BB notes, but different notation. Also, in derivation hidden factor of 2 for light polarizations is replaced by factor of 2 for electron spins)
    * Use de Broglie relation $p_\mathrm{e} = \hbar k = hk/2\pi$:
    $$\mathrm{d}g_\mathrm{e} = \frac{8\pi p_\mathrm{e}^2 \mathrm{d}p_\mathrm{e}}{h^3}\,\mathrm{d}V$$
    * To find $\mathrm{d}V$: if there are n_e electrons per unit volume, then each electron has $\mathrm{d}V = 1/\neq$ available to it:
    $$\mathrm{d}g_\mathrm{e} = \frac{8\pi p_\mathrm{e}^2 \mathrm{d}p_\mathrm{e}}{h^3 n_\mathrm{e}}$$
    (Note: this is a classical-physics fudge, the proper way is to use **Fermi-Dirac statistics** from the start)
- So:
$$\frac{\mathrm{d}N_{i+1}}{N_i} = \frac{g_{i+1,1}}{g_{i,1}} \frac{8\pi p_\mathrm{e}^2 \mathrm{d}p_\mathrm{e}}{h^3 n_\mathrm{e}} e^{-(\chi_i + p_\mathrm{e}^2/2m_\mathrm{e})/kT}$$
- Integrate over all electron momenta to get total number in stage $i+1$:
$$\frac{N_{i+1}}{N_i} = \int \frac{\mathrm{d}N_{i+1}}{N_i} = \frac{g_{i+1,1}}{g_{i,1}} \frac{8\pi}{h^3 n_\mathrm{e}} e^{-\chi_i/kT} \int_0^\infty p_\mathrm{e}^2 e^{p_\mathrm{e}^2/2m_\mathrm{e}kT} \mathrm{d}p_\mathrm{e}$$
- Use identity
$$\int_0^\infty x^2 e^{-a^2x^2} \mathrm{d}x = \frac{\sqrt{\pi}}{4a^3}$$
to get result
$$\frac{N_{i+1}}{N_i} = \frac{2g_{i+1,1}}{n_\mathrm{e} g_{i,1}} \left(\frac{2\pi m_\mathrm{e} kT}{h^2}\right)^{3/2} e^{-\chi_i/kT}$$
- Additional correction: allow for exitation amongst energy levels of each ionization stage $\longrightarrow$ replace $g_{i,1}$ by Z_i and $g_{i+1,1}$ by Z_{i+1}:
$$\frac{N_{i+1}}{N_i} = \frac{2Z_{i+1}}{n_\mathrm{e} Z_i} \left(\frac{2\pi m_\mathrm{e} kT}{h^2}\right)^{3/2} e^{-\chi_i/kT}$$
This is the famous **Saha equation** (sometimes called Saha-Boltzmann equation)