**Problem 7.5.** Consider a system consisting of a single impurity atom/ion in a semiconductor. Suppose that the impurity atom has one "extra" electron compared to the neighboring atoms, as would a phosphorus atom occupying a lattice site in a silicon crystal. The extra electron is then easily removed, leaving behind a positively charged ion. The ionized electron is called a **conduction electron**, because it is free to move through the material; the impurity atom is called a **donor**, because it can "donate" a conduction electron. This system is analogous to the hydrogen atom considered in the previous two problems except that the ionization energy is much less, mainly due to the screening of the ionic charge by the dielectric behavior of the medium.

**(a)** Write down a formula for the probability of a single donor atom being ionized. Do not neglect the fact that the electron, if present, can have two independent spin states. Express your formula in terms of the temperature, the ionization energy $I$, and the chemical potential of the "gas" of ionized electrons.

**(b)** Assuming that the conduction electrons behave like an ordinary ideal gas (with two spin states per particle), write their chemical potential in terms of the number of conduction electrons per unit volume, $N_c/V$.

**(c)** Now assume that every conduction electron comes from an ionized donor atom. In this case the number of conduction electrons is equal to the number of donors that are ionized. Use this condition to derive a quadratic equation for $N_c$ in terms of the number of donor atoms ($N_d$), eliminating $\mu$. Solve for $N_c$ using the quadratic formula. (Hint: It's helpful to introduce some abbreviations for dimensionless quantities. Try $x = N_c/N_d$, $t = kT/I$, and so on.)

**(d)** For phosphorus in silicon, the ionization energy is 0.044 eV. Suppose that there are $10^{17}$ P atoms per cubic centimeter. Using these numbers, calculate and plot the fraction of ionized donors as a function of temperature. Discuss the results.

Phys 335: Problem 7.5 (Ionization of donor atoms)

(a) States:

ionized: $E = 0$, $N = 0$, Gibbs factor $= e^0 = 1$

unionized: $E = -I$, $N = 1$, Gibbs factor: $e^{-(-I-\mu\cdot 1)/kT}$

Grand partition function

$$\mathcal{Z} = 1 + \underset{\uparrow \text{ 2 spins}}{2} e^{-(-I-\mu)/kT}$$

$$P(\text{ionized}) = \frac{1}{\mathcal{Z}} = \frac{1}{1+2e^{-(-I-\mu)/kT}}$$

(b) $$\mu = -kT \ln\left(\frac{V Z_{int}}{N_c N_Q}\right) \qquad (\text{Eq. } 6.93)$$

$Z_{int} = 2$ (2 spins) $\qquad N_c = \#$ of conduction electrons

$$n_Q = \frac{h^3}{(2\pi m kT)^{3/2}} \qquad (\text{but don't put in yet...})$$

$$\mu = -kT \ln\left(\frac{2}{(N_c/V)\cdot n_Q}\right)$$

(c) $N_d = \#$ of donor atoms.

Assume $P(\text{ionized}) = \dfrac{N_c}{N_d}$

$$\frac{N_c}{N_d} = \frac{1}{1+2e^{-(-I-\mu)/kT}} = \frac{1}{1+2e^{I/kT}e^{\mu/kT}}$$

But $$e^{\mu/kT} = e^{-\ln\left(\frac{2}{(N_c/V)\cdot n_Q}\right)} =$$

$$e^{\mu/kT} = e^{\ln\left(\frac{N_c}{V}\cdot n_Q/2\right)} = \frac{N_c}{V}\,\frac{n_Q}{2}$$

$$\therefore \frac{N_c}{N_d} = \frac{1}{1 + 2e^{I/kT} \cdot \frac{N_c}{V}\frac{N_Q}{2}}$$

$$\frac{N_c}{N_d} = \frac{1}{1 + N_c\left(\frac{N_Q}{V}\right)e^{I/kT}}$$

Solve for $N_c$. Take the limit.

$x = \frac{N_c}{N_d}$ $\qquad t = \frac{kT}{I}$

$$x = \frac{1}{1 + N_d \, x \, \frac{N_Q}{V} e^{1/t}}$$

let $y$ = the other non-$x$ stuff

$$y = N_d \frac{N_Q}{V} e^{1/t}$$

$$x = \frac{1}{1 + xy} \Rightarrow yx^2 + x - 1 = 0$$

$$x = \frac{-1 \pm \sqrt{1 + 4y}}{2y}$$

since $x = N_c/N_d$ must be positive,

$$x = \frac{1}{2y}\left(\sqrt{1 + 4y} - 1\right)$$ , plug $y$ back in

$$\frac{N_c}{N_d} = \frac{1}{2N_d\left(\frac{N_Q}{V}\right)e^{1/t}}\left(\sqrt{1 + 4N_d\left(\frac{N_Q}{V}\right)e^{1/t}} - 1\right)$$

to express it all in terms of temperature, recall

$$n_Q = \frac{h^3}{(2\pi m kT)^{3/2}}$$

and $t = kT/I$, so

$$\boxed{\frac{N_c}{N_d} = \frac{1}{2(N_d/V)} \frac{(2\pi m kT)^{3/2}}{e^{I/kT}} \times \left(\sqrt{1 + 4\left(\frac{N_d}{V}\right)\frac{h^3}{(2\pi m kT)^{3/2}} e^{I/kT}} - 1\right)}$$

(d) Put in values and plot $\frac{N_c}{N_d}$ vs temperature.

$$\frac{N_d}{V} = \frac{10^7}{cm^3} \times \left(\frac{10^2 cm}{m}\right)^3 = \frac{10^{13}}{m^3}$$

$I = 0.044 eV$, so $\frac{I}{k} = \frac{0.044 eV}{8.617 \times 10^{-5} eV/K} = 510.6 K$

This gives a scale of relevant temperatures.
The "m" is for an electron.

For plotting, note that writing it in terms of $y$ is simpler

$$x = \frac{N_c}{N_d} = \frac{1}{2y}\left(\sqrt{1+4y} - 1\right)$$

where

$$y = \frac{N_d}{V} n_Q e^{-1/t} = \left(\frac{N_d}{V}\right)\left(\frac{h^3}{(2\pi m kT)^{3/2}}\right) e^{I/kT}$$

$$= \frac{N_d}{V} \left(\frac{h^2}{2\pi m}\right)^{3/2} \cdot \frac{1}{(kT)^{3/2}} e^{I/kT}$$

$$y = \frac{10^{13}}{m^3}\left[\frac{(6.62\times10^{-34}\,J\cdot s)^2}{(2\pi\cdot 9.11\times10^{-31}\,kg)}\right]^{3/2}\cdot\frac{1}{(1.381\times10^{-23}\,J/K)^{3/2}}\left(\frac{e^{\frac{510.6K}{T}}}{T^{3/2}}\right)$$

$$y = \frac{4.14\times10^{-9}\,K^{3/2}}{T^{3/2}}\cdot e^{510.6K/T}$$

Then

$$\frac{N_c}{N_d} = \frac{1}{2y}\left(\sqrt{1+4y}-1\right)$$

See plot. Note that essentially all the donors are ionized well below room temperature.