Degeneracy vs. Energy Level Scaling for Hydrogen

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I explore the relationship between degeneracy and energy for the Hydrogen atom.

The energy levels of the Hydrogen atom from quantum mechanics are given by:

$$E_n = -\frac{E_0}{n^2} \qquad E_0 = \frac{me^4}{2\hbar^2}, \quad n \in \mathbb{Z}^+ \tag{1}$$

in c.g.s. units, where no perturbations are included. The degeneracy of each level is n^2. If it were possible to ignore electron-electron interactions and fill the energy levels following the Pauli Exclusion Principle, a total of $2n^2$ electrons could occupy each E_n, corresponding to one spin-up and one spin-down electron in each of the n^2 states. To make the atom neutral when it has a fixed number of electrons, the charge of the nucleus could be increased, scaling E_0. In this manner, a completely filled shell would contribute $-2E_0$ to the total energy of the system, regardless of the n that the shell corresponds to.

This is consistent with the Hellman-Feynman theorem:

$$\frac{\partial E_n}{\partial e} = \left\langle \psi_n \middle| \frac{\partial H}{\partial e} \middle| \psi_n \right\rangle \rightarrow \left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 n^2} \tag{2}$$

where $a_0 = \frac{\hbar^2}{m_e e^2}$ is the Bohr radius. Higher energy shells of Hydrogen are further away from the proton. Increasing the amount of orbiting electron charge by n^2 would cancel this effect and give the same potential energy for each shell.

The total energy of the system is linear in the filling fraction ν, representing the number of filled energy levels. Each electron within a given shell contributes equally, while a totally filled shell contributes $-2E_0$. Figure 1 shows how the total energy decreases with ν while the density of allowed values of ν increases as $2n^2$ for shells that can hold more electrons. In the ground state, at $T = 0$, the lowest energy levels are filled.

The symmetry of a constant $D_n E_n$, for degeneracy D_n, also effects the relative probability for finding a single electron in an n-shell versus m-shell state. No electron-electron interactions are being ignored, although only relative probabilities are studied since the sum over all levels diverges. If the probability distribution for the state of a single particle can be treated with Maxwell-Boltzmann statistics, then:

$$\frac{\mathbb{P}(n)}{\mathbb{P}(1)} = n^2 e^{\frac{E_0}{k_B T}\left(\frac{1}{n^2} - 1\right)}. \tag{3}$$

In the high temperature limit, $\mathbb{P}(n) \propto n^2$, so that the average contribution to the energy of the system: $\mathbb{P}(n)E_n$ is independent of n.

Equation 3 also shows that $\mathbb{P}(n)$ has a minimum at $n = \sqrt{\frac{E_0}{k_B T}}$, corresponding to $k_B T = \frac{E_0}{n^2} = |E_n|$. When the characteristic thermal energy $k_B T$ is closest to E_n, the n^{th} energy level is least likely to be populated. This relates to stimulated absorption since the amount of thermal energy is just enough to ionize the n^{th} energy level. For instance, a gas of hydrogen atoms (as opposed to H_2) at the temperature of the sun's photosphere would have a minimum relative population for the $n = 5$ energy level according this Boltzmann distribution. Higher temperatures preferentially depopulate shells with smaller n.

If instead, we had a constant $D_n E_n$ with $D_n \propto n^j$ rather than n^2, the least populated state would still correspond to $k_B T = |E_n|$. If the power of the degeneracy is different, such that $D_n \propto n^f$, $E_n \propto n^{-j}$, the minimum population occurs at $k_B T = \frac{j}{f}|E_n|$. A similar extremum occurs for energy levels that are positive and increase with n, reminiscent of Rotational Raman Scattering.

Since degeneracies broken by perturbations usually only cause small splittings in the energy levels of a system, one could imagine that there would be cases where the $\frac{j}{f}$ proportionality factor could be used to define an effective order for the degeneracy of energy levels.

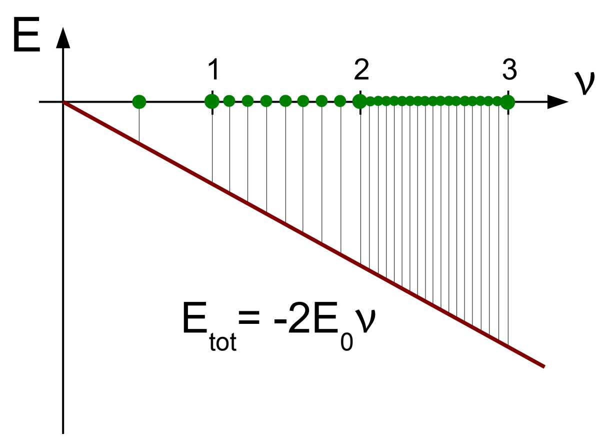

FIG. 1. Total energy as a function of the filling fraction for the ground state of an idealized multi-electron atom.