University of Washington
Department of Chemistry
Chemistry 453
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Lecture 19 3/02/15
Recommended Reading: Atkins & DePaula: 9.7-9.8

A. Electron Motions & Partition Functions

- Quantifying the orbital motion of the electron requires three variable quantities; the distance of the electron from the nucleus r, and two angles θ and φ. Three physical variables requires three quantum numbers.
- Unlike the rigid rotor, the distance r can vary for the electron and in early quantum theory r corresponded to the radius of a circular electron orbital in the hydrogen atom. Such a simple description does not apply to multi-electron atoms however.
- We learned in Chemistry 152 that for single electron atoms (i.e. hydrogen) the orbital energy is given by

$$E_n = -\frac{\Re}{n^2} \tag{19.1}$$

- In equation 17.1 $\Re = \frac{m_e e^4}{8\varepsilon_0^2 h^2} = 2.18\times 10^{-18}\,J$ is called the Rydberg constant

and the principal quantum number which quantizes the energy is n=1,2,3,4...

- In addition, as in the rigid rotor, the total orbital angular momentum L of the electron and the z component of the orbital angular momentum L_z are quantized according to:

$$\begin{aligned} L^2 &= \hbar^2 \ell(\ell+1); \quad \ell = 0,1,2\ldots n-1 \\ L_z &= \hbar m; \quad m = -\ell, -\ell+1, \ldots, \ell-1, \ell \end{aligned} \tag{19.2}$$

- In accordance with these three quantization rules the atomic wave function for a single electron atom has the form:

$$\psi_{n,\ell,m}(r,\theta,\varphi) = R_{n\ell}(r) Y_{\ell m}(\theta,\varphi) = R_{n\ell}(r)\Theta_{\ell m}(\theta)\Phi_m(\varphi) \tag{19.3}$$

where the spherical harmonics $Y_{\ell m}(\theta,\varphi)$ are the wave functions for the rigid rotor problem. The radial wave function $R_{n\ell}(r)$ arises in the hydrogen atom because r is no longer fixed.

- As a result of equations 19.1-19.3, orbital energies are degenerate. Based on the quantization rules given in equation 19.2 the following energies and degeneracies as a function of n are:

N quantum number	1	2	3	4
Energy (units –R)	1	1/4	1/9	1/16
Degeneracy (no spin)	1	4	9	16
Degeneracy (with spin)	2	8	18	32

Table 19.1: Orbital energies and degeneracies for the hydrogen atom

- The degeneracy is calculated in the following way.
  - For n=1, $\ell = 0$, m=0
  - For n=2, $\ell = 0$, m=0; $\ell = 1$, m=-1,0,+1
  - For n=3, $\ell = 0$, m=0; $\ell = 1$, m=-1,0,+1; $\ell = 2$, m=-2,-1,0,+1,+2
- This appears to result in a degeneracy of n^2. But in addition to degeneracy arising from orbital angular momentum, the electron possesses a second type of angular momentum called spin angular momentum. Spin angular momentum was once proposed to originate from the spinning of the electron, conceived to be a sphere of negative charge, around its polar axis. This picture is appealing but wrong. Spin angular momentum is a purely quantum mechanical property, which has no classical analog.
- For all n, the total spin angular momentum of the electron is

$$S^2 = \hbar^2 s(s+1) \text{ where } s = \tfrac{1}{2}. \quad (19.4)$$

- In addition the z component of the spin angular momentum is quantized:

$$S_Z = \hbar m_s \text{ where } m_s = \pm\tfrac{1}{2} \quad (19.5)$$

- Because of the spin angular momentum the degeneracy is doubled and for single electron atoms is $g_n = 2n^2$. See table 17.1.
- With these consideration the electronic partition function for a single electron atom is:

$$q_{elec} = \sum_{n=1}^{\infty} g_n e^{-E_n/k_BT} = e^{-E_1/k_BT}\sum_{n=1}^{\infty} g_n e^{-(E_n-E_1)/k_BT} = e^{-E_1/k_BT}\sum_{n=1}^{\infty} g_n e^{-\Delta E_{n,1}/k_BT} =$$
$$e^{-E_1/k_BT}\sum_{n=1}^{\infty} g_n e^{\Re\left(\frac{1}{n^2}-1\right)/k_BT} = q' e^{-E_1/k_BT} \quad (19.6)$$

- $\Re = 2.18\times10^{-18}\,J$ so assuming T=1000K then $k_BT=1.38\times10^{-20}J$. Then $\frac{\Re}{k_BT} = \frac{2.18\times10^{-18}}{1.38\times10^{-20}} \approx 158$. The first few terms of the expansion are

$$q_{elec} = e^{-E_1/k_BT}\left(g_1 + g_2e^{-119} + g_3e^{-141} + \ldots\right) = e^{-E_1/k_BT}\left(2 + 8e^{-119} + 18e^{-141} + \ldots\right) \approx 2e^{-E_1/k_BT} \quad (19.7)$$

- For most atoms the energy splittings ΔE are so large that only the ground electronic state is populated so that $q' \approx g_1$. It is always possible to reference the lowest energy level as "zero" thus making the electronic partition function simply $q_{elec}=g_1$.
- Multi-electron atoms do not follow the simple energies and degeneracies of single electron atoms. A table of atomic energies and degeneracies for atoms is given in Table 15.2. In general the partition function of a monatomic atom is: $q = q_{trans}q_{elec} = \frac{V}{h^3}\left(2\pi m k_BT\right)^{3/2}\left(g_1 + g_2e^{-\Delta E_{2,1}/k_BT} + \ldots\right)$
- Then the internal energy is:

$$U = k_BT^2\frac{\partial \ln Q}{\partial T} = \frac{3}{2}Nk_BT + \frac{Ng_2\Delta E_{2,1}e^{-\Delta E_{2,1}/k_BT}}{q_{elec}} \quad (19.8)$$

- Note because $\Delta E_{2,1} >> k_B T$, the second term is small compared to the first and electron motions make a very small contribution to the internal energy. Now the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \frac{3}{2} N k_B + \frac{N k_B g_2}{q_{elec}} \left(\frac{\Delta E_{2,1}}{k_B T} \right)^2 e^{-\Delta E_{2,1}/k_B T} \approx \frac{3}{2} N k_B \qquad (19.9)$$

- Again, the exponential in the second term in equation 17.9 makes the electronic contribution to the heat capacity vanishingly small.