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 $\theta$ and $\varphi$. 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
  \[ E_n = -\frac{\mathcal{R}}{n^2} \] (19.1)

  - In equation 17.1, $\mathcal{R} = \frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} = 2.18 \times 10^{-18} \text{ J}$ 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:
  \[ L^2 = \hbar^2 \ell (\ell + 1); \quad \ell = 0, 1, 2...n - 1 \]
  \[ L_z = \hbar m; \quad m = -\ell, -\ell + 1, ..., \ell - 1, \ell \] (19.2)

- In accordance with these three quantization rules the atomic wave function for a single electron atom has the form:
  \[ \psi_{n,\ell,m}(r,\theta,\varphi) = R_{n\ell}(r) Y_{\ell m}(\theta,\varphi) \Theta_{\ell m}(\theta) \Phi_{m}(\varphi) \] (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:

<table>
<thead>
<tr>
<th>$n$ quantum number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (units –R)</td>
<td>1</td>
<td>1/4</td>
<td>1/9</td>
<td>1/16</td>
</tr>
<tr>
<td>Degeneracy (no spin)</td>
<td>1</td>
<td>4</td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>Degeneracy (with spin)</td>
<td>2</td>
<td>8</td>
<td>18</td>
<td>32</td>
</tr>
</tbody>
</table>
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
  \[ S^2 = \hbar^2\left(s + \frac{1}{2}\right) \]  
   \[ \text{(19.4)} \]
- In addition the z component of the spin angular momentum is quantized:
  \[ S_z = \hbar m_s \text{ where } m_s = \pm \frac{1}{2} \]  
   \[ \text{(19.5)} \]
- 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 considerations the electronic partition function for a single electron atom is:
  \[ q_{elec} = \sum_{n=1}^{\infty} g_n e^{-E_n/k_BT} = e^{-E_1/k_BT} \sum_{n=1}^{\infty} g_n e^{-\Delta E_{n1}/k_BT} = e^{-E_1/k_BT} \sum_{n=1}^{\infty} g_n e^{-\Delta E_{n1}/k_BT} = q'e^{-E_1/k_BT} \]  
   \[ \text{(19.6)} \]
- \( \Re = 2.18 \times 10^{-18} J \) so assuming \( T=1000K \) then \( k_BT=1.38 \times 10^{-20} J \). Then
  \[ \frac{\Re}{k_BT} = \frac{2.18 \times 10^{-18}}{1.38 \times 10^{-20}} \approx 158. \]  
   The first few terms of the expansion are
  \[ q_{elec} = e^{-E_1/k_BT} \left(g_1 + g_2 e^{-119} + g_3 e^{-141} + \ldots \right) = e^{-E_1/k_BT} \left(2 + 8e^{-119} + 18e^{-141} + \ldots \right) \approx 2e^{-E_1/k_BT} \]  
   \[ \text{(19.7)} \]
- For most atoms the energy splittings \( \Delta E \) 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:
  \[ q = q_{trans} q_{elec} = \frac{V}{\hbar^2} \left(2\pi mk_BT\right)^{3/2} \left(g_1 + g_2 e^{-\Delta E_{21}/k_BT} + \ldots \right) \]
- Then the internal energy is:
  \[ U = k_BT^2 \frac{\partial \ln Q}{\partial T} = 3 \frac{Nk_BT}{2} + \frac{Ng_2\Delta E_{21} e^{-\Delta E_{21}/k_BT}}{q_{elec}} \]  
   \[ \text{(19.8)} \]
• Note because $\Delta E_{2,1} \gg k_B T$, 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:

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

(19.9)

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