From the preceding discussion, it should be clear that one cannot talk about high or low temperatures without qualifying which mode or modes are meant.

Exercise 15. Verify the low and high temperature asymptotes represented in Fig. IIIC-3 by applying the corresponding limits to the vibrational specific heat function (see Exer. 13).

$$\bar{c}_{v,v} = \bar{R}\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T}-1\right)^2}$$

Hint: Use the fact that $e^x \Rightarrow \infty$ as $x \Rightarrow \infty$ and $e^x = 1 + x$ as $x \Rightarrow 0$.

D. Electronic (Dissociation) Mode

The bound electrons of an atom are tied to its nucleus by coulombic attraction. For a *single electron (hydrogen) atom* the Schroedinger equation can be solved to obtain the electronic energy levels and their degeneracy.

$$\varepsilon_{el,H}(\ell) = B_{el,H} f_{el}(\ell) \qquad B_{el,H} = \frac{e^4 m_e^*}{8\varepsilon_o^2 h^2} \qquad f_{el,H}(\ell) = -\frac{1}{\ell^2} \qquad g_{el,H}(\ell) = 2\ell^2 \qquad \ell = 1,2,3,..,$$

in which θ is the charge, m_e^* is the rest mass of the elctron, and ε_o is the permittivity of free space. Notice that the minimum, ground level, energy is negative. Work must be done to remove the electron from the atom. That is, energy must be added to ionize the atom. The electronic characteristic temperature of a hydrogen atom is

$$\theta_{el,H} = \frac{B_{el,H}}{k} = \frac{e^4 m_e^*}{8\varepsilon_o^2 h^2 k}$$

Exercise 16. Determine the magnitude of the electronic characteristic temperature of a hydrogen atom.

The solution of Exer. 16 shows that $\theta_{el,H} \sim 10^5$K. Thus even at combustion level temperatures, a hydrogen atom's electronic mode is unexcited. It would contribute no more than a constant to properties, and nothing to property changes.

A solution of the Schroedinger equation for a multielectron atom requires that repulsion between the like charge electrons be accounted for in addition to their attraction to the nucleus. This problem is as yet too difficult for exact analytic solution. Analysis of a molecule is even more difficult, as the electrons are then repelled by one another and attracted to all of the nuclei, simultaneously. Thus neither the level series nor θ_{el} can be analytically determined for particles that are more complex than the one electron atom, viz., the hydrogen atom. Instead these parameters are inferred from spectroscopic measurement.[18] A study of these data shows that the magnitude determined for a

[18]Since the magnitudes of θ_{el} are quite high, only the first few levels are needed. The parameters required for the rotational and vibrational modes are also obtained spectroscopically $\hat{\theta}_r$, $\theta_{v,p}$. But since the model is valid only a single parameter is needed.