a solution of the Schroedinger equation (Refs. 1, 4 or 5). In terms of its single moment of inertia ($I = I_x = I_y$; $I_z = 0$), the results, written in the form of eqn. IIIC-12, are

$$\varepsilon_{r,\ell} = B_r f_r(\ell) \qquad B_r = \frac{h^2}{8\pi^2 I} \qquad f_r(\ell) = \ell(\ell+1) \qquad g_r(\ell) = (2\ell+1) \qquad \ell = 0,1,2,3,\ldots,$$

Notice that this quantum number series, ℓ, begins with zero, and that the minimum rotational energy is zero, i.e., no rotation. Following our procedure, the rotational characteristic temperature is defined by (eqn. IIIC-13)

$$\theta_r = \frac{B_r}{k} = \frac{h^2}{8\pi^2 Ik}$$

Notice that θ_r is based on the only nonzero moment of the linear rotator. This corresponds to the principal, largest moment of linear molecules. Linear molecules include all diatomic molecules and polyatomic molecules whose atoms form a single line.

The values of θ_r for a number of diatomic and linear polyatomic molecules are listed in Table IIIC-2. All of them are much larger than the translational characteristic temperatures of the preceding section.[9] However, when we compare each substance's θ_r to its region of gaseous states, we conclude that only hydrogen and a few of the lighter hydrogen compounds have characteristic temperatures high enough that they exist in the gaseous state at temperatures on the order of θ_r. Thus, the rotational states of the vast majority of diatomic gases need only be considered in the high temperature limit, $T \gg \theta_r$. The following example develops the rotational partition function for linear rotators in this limit.

Example 7. Evaluate the rotational partition function of a rigid linear rotator in the high temperature limit, $T \gg \theta_r$.

In the high-temperature limit the partition function sum is accurately approximated by an integral

$$Z_r = \sum_{\ell=0}^{\infty} (2\ell+1)e^{-\ell(\ell+1)\theta_r/T} = \int_0^{\infty} (2\ell+1)e^{-\ell(\ell+1)\theta_r/T}\, d\ell$$

Evaluation of this integral is facilitated with the transformation, $\xi \equiv \ell(\ell+1)$, $d\xi = (2\ell+1)d\ell$, $\xi = 0$ when $\ell = 0$ and $\xi = \infty$ as $\ell \to \infty$. Thus,

$$Z_r = \int_0^{\infty} e^{-\xi\theta_r/T}\, d\xi = \frac{T}{\theta_r}$$

From Exmp. 7 the partition function and (using eqn. IIIC-10) the probability distribution for *linear rotators in the high temperature limit* are

$$Z_r = \frac{T}{\theta_r} \qquad \rho_{r,\ell} = \frac{\theta_r(2\ell+1)e^{-\ell(\ell+1)\theta_r/T}}{T}$$

[9]The fact that $\theta_r \gg \theta_{tr}$ indicates that the spacing between rotational levels is much larger than that between translational levels. By comparison, the translational energy is almost continuous.