Exercise 6. Helium has the lowest normal boiling temperature, 4.22 K, and is therefore the most likely gas to be encountered under conditions that violate the indistinguishable limit. What is the value of $n_j/g_j|_{max}$ at its normal boiling point? If $n_j/g_j|_{max} = 10^{-2}$ part/state is accepted as a boundary of the indistinguishable limit, at what temperature would helium gas cross that boundary at atmospheric pressure?

The solution of Exer. 6 demonstrates that helium gas violates the indistinguishable limit at temperatures near its normal boiling point. The normal isotope of helium, He^4, is a Boson. Its unique separation into two liquid phases is a result of what is called a *Bose degeneracy*, occurring when this system leaves the indistinguishable limit.

The translational (external) mode accounts for the motion of a gas molecule—our particle. We have restricted our efforts to determining its contribution to the partition function and properties, leaving detailed consideration of the distribution of particles among the translational energy levels, $\rho_{tr,j}$, for Unit IIIE. In that unit we will see that the speed distribution is a principal input to the determination of the transport properties of gases. In the following section we begin consideration of the particle's internal modes. These account for the motions of the atoms within the molecule relative to its center of gravity, as well as the motions of the electrons and nuclei within the atom relative to its center of gravity. We begin with molecular rotation.

B. The Rotational (and Nuclear Spin) Mode

A principal internal mode is the rotation of the molecule about its center of gravity. The rotational components of a molecule can be resolved into its three principal moments of inertia, I_x, I_y and I_z. For simplicity we first consider linear molecules, $I_x = I_y >> I_z$ (see Fig. IIIC-1). The energy levels and degeneracy for *linear rotators* are obtained from

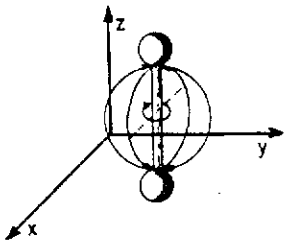

Fig. IIIC-1. Rotation of Components of a Linear Molecule

Ans. 3.

$$\bar{u}_{tr} = \bar{R}T^2\left[\frac{\partial \ln Z_{tr}(T,\eta\bar{v})}{\partial T}\right]_{\bar{v}} = \bar{R}T^2\left\{\frac{\partial}{\partial T}\ln\left[\eta\bar{v}\left(\frac{2\pi M\bar{R}T}{(N_A h)^2}\right)^{3/2}\right]\right\}_{\bar{v}} = \bar{R}T^2\,\frac{3}{2}\left(\frac{1}{T}\right) = \frac{3}{2}\bar{R}T$$

and

$$\bar{c}_{v,tr} = \left(\frac{\partial \bar{u}_{tr}}{\partial T}\right)_{\bar{v}} = \frac{3}{2}\bar{R}$$

Ans. 4.

$$\bar{h}_{tr} = \bar{u}_{tr} + p_{tr}\bar{v} = \frac{3}{2}\bar{R}T + \left(\frac{\bar{R}T}{\bar{v}}\right)\bar{v} = \frac{5}{2}\bar{R}T$$

Ans. 5.

$$\bar{s}_{ex} = \bar{s}_{tr} = \frac{\bar{u}_{tr}}{T} + \bar{R}\ln\left(\frac{Z_{tr}}{\eta N_A}\right) + \bar{R} = \frac{3}{2}\frac{\bar{R}T}{T} + \bar{R}\ln\left[\left(\frac{kT}{p}\right)\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2}\right] + \bar{R}$$

$$= \bar{R}\left\{\frac{5}{2} + \ln\left[\left(\frac{kT}{p}\right)^{5/2}\left(\frac{2\pi m^*}{h^2}\right)^{3/2}\right]\right\}$$