Explain σ

$$Z_r = \frac{\pi}{\sigma}\left(\frac{T}{\hat{\theta}_r}\right)^{3/2} \quad \text{where} \quad \hat{\theta}_r = \left(\theta_{r,x} \cdot \theta_{r,y} \cdot \theta_{r,z}\right)^{1/3}$$

Values of $\hat{\theta}_r$ for a number of nonlinear molecules are included in Table IIIC-2.

The preceding paragraphs modeled linear molecules as rigid linear rotators ($I_x = I_y = I$, $I_z = 0$). Clearly, this is an approximation. The moment of inertia for rotation about the molecular line of centers (the z axis of Fig. IIIC-1) is not zero; it is only very small. This moment is essentially the sum of the moments of the in-line atoms for "nuclear spin." (Even though the electron orbital radii are comparatively large their mass is low enough that they do not appreciably affect the moment.) Nuclear radii are extremely small in comparison to intermolecular spacing, therefore the nuclear spin moment is many orders smaller than the molecular moment. Noting that θ_r is inversely proportional to the moment of inertia, the fact that $\theta_{ns} \sim 10^{10}$K should not be surprising. Thus, nuclear spin is not excited except at extremely high temperatures.[10]

Insofar as nuclear spin is independent of molecular rotation, the determination of the effect of spin on properties is a simple matter. But for molecules with one or more rotational symmetry axis, they are not independent. For example, consider diatomic molecule elements.

Molecular Rotation-Nuclear Spin Coupling. Diatomic molecule elements are composed of two identical atoms. Such molecules are called *homonuclear*. The identical nuclei of homonuclear diatomic molecules are indistinguishable particles within the molecule. If these nuclei have an odd number of protons and neutrons, they are Fermions (e.g., hydrogen with a single proton). If they have an even number, they are Bosons (e.g., deuterium with one proton and one neutron). It was noted briefly in Sect. IIB of Unit IIIA that Fermions have antisymmetric wave functions with respect to an exchange of identical particles and Bosons have symmetric wave functions. Further, when the ends of a diatomic molecule are exchanged, it reverses both its spin and its rotation. Thus the states of these separate modes are altered simultaneously by an exchange of identical nuclei . They are coupled and the product of the spin and rotational wave function must be even or odd depending upon the character of the nuclei. For example, if the nuclei are Fermions, then rotational states with an even wave function require a simultaneous spin state of odd wave function, and vice versa.

As explained above, rotational-nuclear spin coupling complicates the determination of the partition function and properties of the rotational-nuclear spin modes of molecules with rotational symmetry, particularly in the range, $T \sim \theta_r$. But the only symmetric molecules that are gases in this range are hydrogen and deuterium. Indeed, rotation-spin coupling is the basis of the distinction between ortho and para hydrogen. In the interest of simplicity, we forego explicit consideration of the general case(see Ref. 1, 4 or 5), but will consider only the high temperature limit of rotation-nuclear spin coupling. In this

[10]There are instances, e.g., nuclear magnetic resonance (NMR) spectroscopy in which nuclear excitation is magnetically induced.