

7-32. Consider a two-dimensional harmonic oscillator with Hamiltonian

$$H = \frac{1}{2m} (p_x^2 + p_y^2) + \frac{k}{2} (x^2 + y^2)$$

According to the principle of equipartition of energy, the average energy will be $2kT$. Now transform this Hamiltonian to plane polar coordinates to get

$$H = \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{k}{2} r^2$$

What would you predict for the average energy now? Show by direct integration in plane polar coordinates that $\bar{\epsilon} = 2kT$. Is anything wrong here? Why not?

8-15. The classical rotational kinetic energy of a symmetric top molecule is

$$K = \frac{p_\theta^2}{2I_A} + \frac{(p_\phi - p_\psi \cos \theta)^2}{2I_A \sin^2 \theta} + \frac{p_\psi^2}{2I_C}$$

where I_A , I_A , and I_C are the principal moments of inertia, and θ , ϕ , and ψ are the three Euler angles. Derive the classical limit of the rotational partition function for a symmetric top molecule. Hint: Recall that the Euler angles have the ranges:

$$0 \leq \theta \leq \pi$$

$$0 \leq \phi \leq 2\pi$$

$$0 \leq \psi \leq 2\pi$$

8-16. The classical Hamiltonian for an asymmetric top molecule with principal moments of inertia I_A , I_B , and I_C is given by

$$H = \frac{1}{2I_A \sin^2 \theta} \{ (p_\phi - p_\psi \cos \theta) \cos \psi - p_\theta \sin \theta \sin \psi \}^2 \\ + \frac{1}{2I_B \sin^2 \theta} \{ (p_\phi - p_\psi \cos \theta) \sin \psi + p_\theta \sin \theta \cos \psi \}^2 + \frac{1}{2I_C} p_\psi^2$$

Derive the classical limit of the rotational partition function for an asymmetric top molecule. Hint: It may help to rearrange the Hamiltonian and integrate over p_θ , p_ϕ , p_ψ in that order.